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Destructive Hydrogenation of Abietic Acid

A Thesis

by

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INTRODUCTION

In many of the foreign countries where the supply of petroleum is definitely limited or completely exhausted, it has been necessary to obtain liquid fuels from other natural resources, principally coal. In this country, however, we are fortunate enough to have available large supplies of petroleum and due to the scientific developments which have taken place in the past decade concerning the methods of prospecting, recovering, refining and utilizing the crude oil we now have available a larger supply than ever before in the history of the country. On the other hand with the enormous increase of mechanized units requiring liquid fuels and the continual demand for higher grade fuels we can not afford to neglect the scientific aspects of any process which is used for the transformation of coal into oil.

Probably the most common of all the processes in use today is coal hydrogenation. Theoretically this is a process involving a large number of hydrogenation and cracking reactions. The first principal reaction is believed to be a hydrogenation of the large complex coal polymer resulting in the reduction in size of the polymer without essentially changing the general character of its unit. The next reaction is a saturation with

hydrogen of the aromatic or unsaturated naphthenic units. These saturated structures are more susceptible to cracking with the result of a broken ring structure and a parafin side chain which then may or may not be separated from the parent unit depending upon the conditions of the reaction. If the severance of the side chain does take place it is saturated by hydrogenation. This cycle of hydrogenation, cracking and hydrogenation continues until the resultant units are stable to the conditions of the reaction or until the products are removed from the process.

At the present time considerable data are available regarding the various coals, catalysts and conditions used in the process as well as the nature of the resulting products. However, the interpretation of the data is greatly handicapped due to the lack of knowledge regarding the mechanism of the reaction. In order to study this mechanism it is necessary to consider the destructive hydrogenation of pure organic compounds. The British Fuel Research Board has realized the importance of this type of work and has already studied such compounds as benzene, naphthalene, anthracene and their homologues. In carrying out their work they have been gradually increasing the complexity of the compounds studied with the ultimate goal of working with a polynuclear structure as closely related to that found in coal as possible.

The present work has to deal with the destructive

hydrogenation of abietic acid under conditions similar to those used in coal hydrogenation but without the use of an added catalyst. However, it is known that iron and other metals in the wall of the retort act as a catalyst. Since this compound is a partially saturated phenanthrene derivative containing a carboxyl as well as two different alkyl side chains its destructive hydrogenation should supply data concerning complete saturation, oxygen removal, alkyl and possibly alicyclic decomposition. The structure of the compound also places it next in complexity to those already studied by the British Fuel Research Board.

It is beyond the scope of this thesis to present a complete picture of the mechanism of coal hydrogenation because the field of possible compounds to be studied is large, the conditions used cover a wide range and the number of catalysts is practically unlimited. However, if and when the complete picture is ever presented it can only be hoped that the present work may be of some use.

ABIETIC ACID, ITS STRUCTURE AND PREPARATION.

The existing literature concerning the resin acids and their physical constants is rather confusing and contradictory. This may be due to the fact that there are so many possible isomers of the same general formula $C_{20}H_{30}O_2$ or to the fact that the acids have a strong tendency to oxidize even at atmospheric conditions. Of all the resin acids, abietic is probably the best known because the others are converted into it under the influence of heat and mineral acids(15). Although the acid is obtained from wood resin by suitable treatment to be explained later it is not an original constituent of the tree secretions.

Fieser (18) presents a rather complete summary of the work up to 1935 on the determination of the structure of abietic acid. He first of all shows the relation of the acid to retene (Fig. 1) by dehydrogenating it with sulfur, selenium (13) and palladium charcoal (46). This accounts for 18 of the 20 carbon

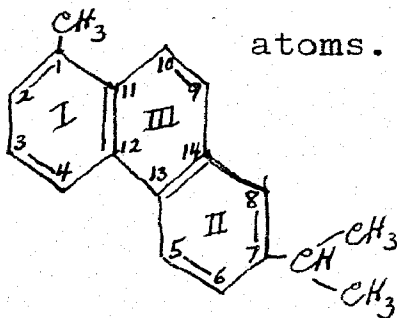


Fig. 1 - Retene

One of the other atoms is of course present as a carboxyl group and the remaining one is removed in the dehydrogenation with sulfur as methyl mercaptan. This indicates its presence as a methyl group situated in either the C₁₁, 12, 13 or 14 position. By the extensive oxidation of the acid with permanganate and the complete analysis of the products, Ruzicka (40) has been able to prove that the methyl group belongs in the C₁₂ position.

The most difficult part in the determination of the structure was the location of the carboxyl group even though it was generally agreed to be present in ring No. 1. The thorough investigation (43) concerning the reduction of the ethyl ester by the Bouveault Method followed by dehydration with phosphorous pentachloride and dehydrogenation with sulfur to form "methylretene" indicated that the carboxyl group could occupy a position on the phenanthrene nucleus, preferably in the C₂ or C₄ position. However, Ruzicka (41), Vocke (53) and Hawarth (25) working independently presented evidence of a tertiary carboxyl group located at the C₁ position with the methyl group. This was especially evident when Ruzicka (41) was able to prove that the so-called "methylretene" was actually a 1 ethyl 7 isopropylphenanthrene.

The addition of hydrogen bromide, accomplished by Levy (36) and the isolation of a dihydroxy acid by Ruzicka and Meyer (44) indicated the presence of unsaturation. Later work by LaLande (31) with permanganate and halogens substantiated the above results and more extensive studies have proved that there are two ethylenic linkages. However, the exact location of the linkages has as yet not been definitely established. More recent work (26) (30) with maleic anhydride has indicated that the double bonds are in conjugate positions and the authorities (45) (19) in the field agree that the bonds are located in the 9, 14 and 7, 8 or 5, 13 positions thus giving the structure as shown in figure 2.

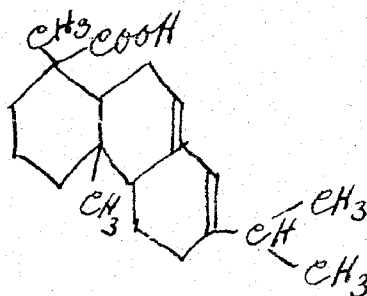


Fig. 2 - Abietic Acid

The early methods for the conversion of rosin into abietic acid were based upon the hydration theory. This theory assumed that the acid was present in the rosin as the anhydride and that the treatment of the rosin with aqueous mineral acid solutions or aqueous solvent solutions converted the anhydride

into the acid. However, this theory was disproved by Fonrobert (21) who was able to show that the true anhydride has entirely different properties from the rosin itself. Ruzicka and Meyer (42) also disproved the theory by perfecting a method of preparing the acid by a vacuum distillation of the rosin. From this it appeared that the preparation was a matter of isomerization which could be accomplished both by heating and by treating the rosin with acids. Thus the methods using the mildest conditions are regarded as the most reliable.

Of the early methods used (37) (35) (12) (28) that of Steele (48) is considered to be the most reliable and convenient. It is the method used by the large majority of workers in the determination of the structure of the acid and consists of refluxing the rosin with 98% acetic acid for two hours, filtering, seeding the solution, allowing the acid to crystallize, separating the crystals and washing with 90% alcohol. After this has been repeated the second or third time the crystals are dried in a vacuum. LaLande (32) has modified Steele's method by recrystallizing the acid several times from 95% alcohol and keeping the solutions stored under nitrogen during the recrystallizations.

Other attempts have been made (39) (22) to prepare the pure l-abietic acid by precipitating the acid with alkali and recovering it, by subsequent sublimation, by isomerization with various acids, vacuum distillation and fractional

recrystallization but the results showed that in most cases it is practically impossible to separate the racemic mixture. Fieser (19) however has suggested that if the acid is to be stored for any length of time it should be done in the form of the sodium tetra abietate salt and that the acid be regenerated as needed. This salt is supposed to be more stable to oxidation.

The acid used for the preliminary runs in the present work was prepared from the Hercules F F Wood Rosin using the LaLande modification of Steele's method. However, for the actual runs reported we were fortunate enough to obtain a large fresh sample of the Hercules Commercial Abietic Acid. This acid was purified by recrystallizing it three times from 90% ethanol. During each recrystallization the solution was stored in a desiccator under nitrogen and in a refrigerator. After the third recrystallization the crystals were dried in a vacuum over anhydrous calcium chloride at 65°C for a period of three hours, weighed and placed immediately into the hydrogenation retort under hydrogen. It was necessary to start with 350 grams of the commercial acid in order to obtain at least 100 grams of the purified acid. In most cases approximately 125 grams of the purified acid was obtained. 100 grams were used in the hydrogenation and the remainder was used to determine the melting point of the batch and in some cases the acid number and ultimate analysis.

In all, eight hydrogenations were made requiring eight batches of acid. The melting point of each of the batches did not vary more than three degrees. The acid was heated from room temperature and would soften between 152-155°C and become a perfectly clear liquid at 157-159°C. LaLande's acid had a melting point of 158°C. The acid number for several of the batches ranged from 178.1 to 187.4 and the percentage carbon and hydrogen of fresh samples varied as follows:

	By Analysis	Theoretical
% C	79.30 - 79.35	79.40
% H	9.89 - 9.90	10.00

It was observed that if the acid remained in the laboratory, eventhough it was stored in a desiccator, for several weeks the acid number would be considerably higher, around 198, the percentages of carbon and hydrogen would decrease, and the melting point would vary over a wider range. This indicated that some oxidation had taken place.

PROCEDURE AND APPARATUS

After the pure abietic acid crystals had been obtained by recrystallization and dried in a vacuum oven over anhydrous calcium chloride, 100 grams were placed immediately in the hydrogenation retort with the stirrer and sealed under hydrogen. The retort is a rotary type of approximately $1\frac{1}{2}$ liters capacity constructed of acid resistant alloy steel. It has an outside diameter of 6 inches and a wall thickness of $1\frac{1}{2}$ inches. It is 14 inches long including the head. The head post and nuts are made of Nirosta steel and the head bolts of chromium steel. The seal between the head of the retort and the retort itself is made by means of copper gaskets in both positions and the valves used to charge the hydrogen and bleed the reaction gases are made according to the specifications published by the Fixed Nitrogen Laboratory (14). The stirrer is made of alloy steel and operates due to the rotation of the retort.

After the acid was placed in the retort, the retort was flushed several times with hydrogen to be sure that all the air had been removed and the pressure brought to between 1900 and 1975 pounds per square inch. It was then stored at this pressure and at room temperature over night while the furnace was being heated. Figure 3 shows a photograph of the furnace and the assembled retort.

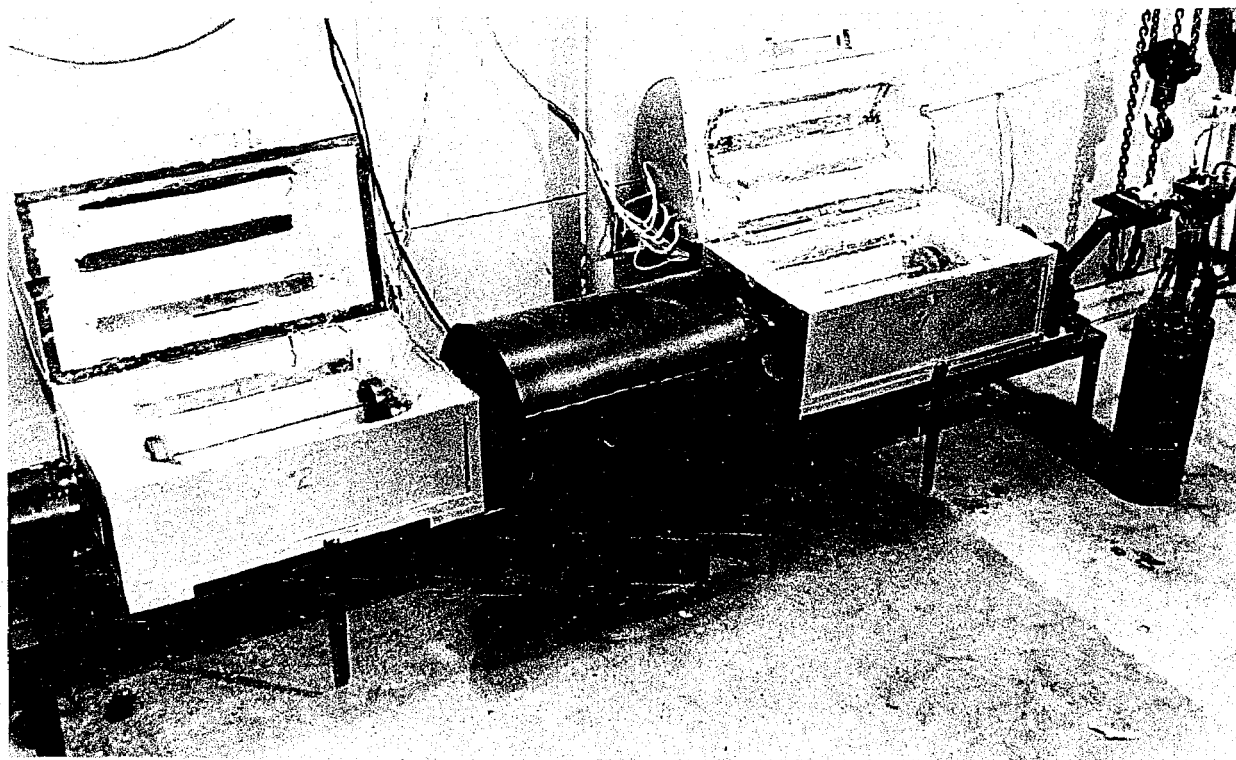


Figure 3

The next morning the pressure was checked to be sure that there were no leaks in the system. The retort was placed in the furnace by means of a hand-operated crane and heated to the desired temperature while being rotated in the furnace. The rate of rotation was approximately 18 revolutions per minute. The temperature was measured by means of an iron-constantan thermocouple which extended down thru the head to the center of the retort. The thermocouple was calibrated in position against a secondary standard iron-

constantan couple which in turn had been calibrated against a platinum-platinum 13% rhodium couple standardized by the U. S. Bureau of Standards.

The time required to heat the retort to its hydrogenation temperature varied from 1 hour and 20 minutes to 2 hours and 10 minutes depending upon the temperature desired. After the hydrogenation temperature (325°C , 370°C , 400°C , 425°C or 450°C) had been obtained the retort was held at this temperature within $\pm 4^{\circ}\text{C}$ for an additional 2 hours. However several runs were conducted at 400°C for a one hour period. At the end of the hydrogenation period the retort was cooled as quickly as possible to about 200°C by blowing air over it. Then it was transferred by means of the crane to a holder and jacketed by an electric heated cover used to hold the retort at 150°C while the reaction gases were being removed.

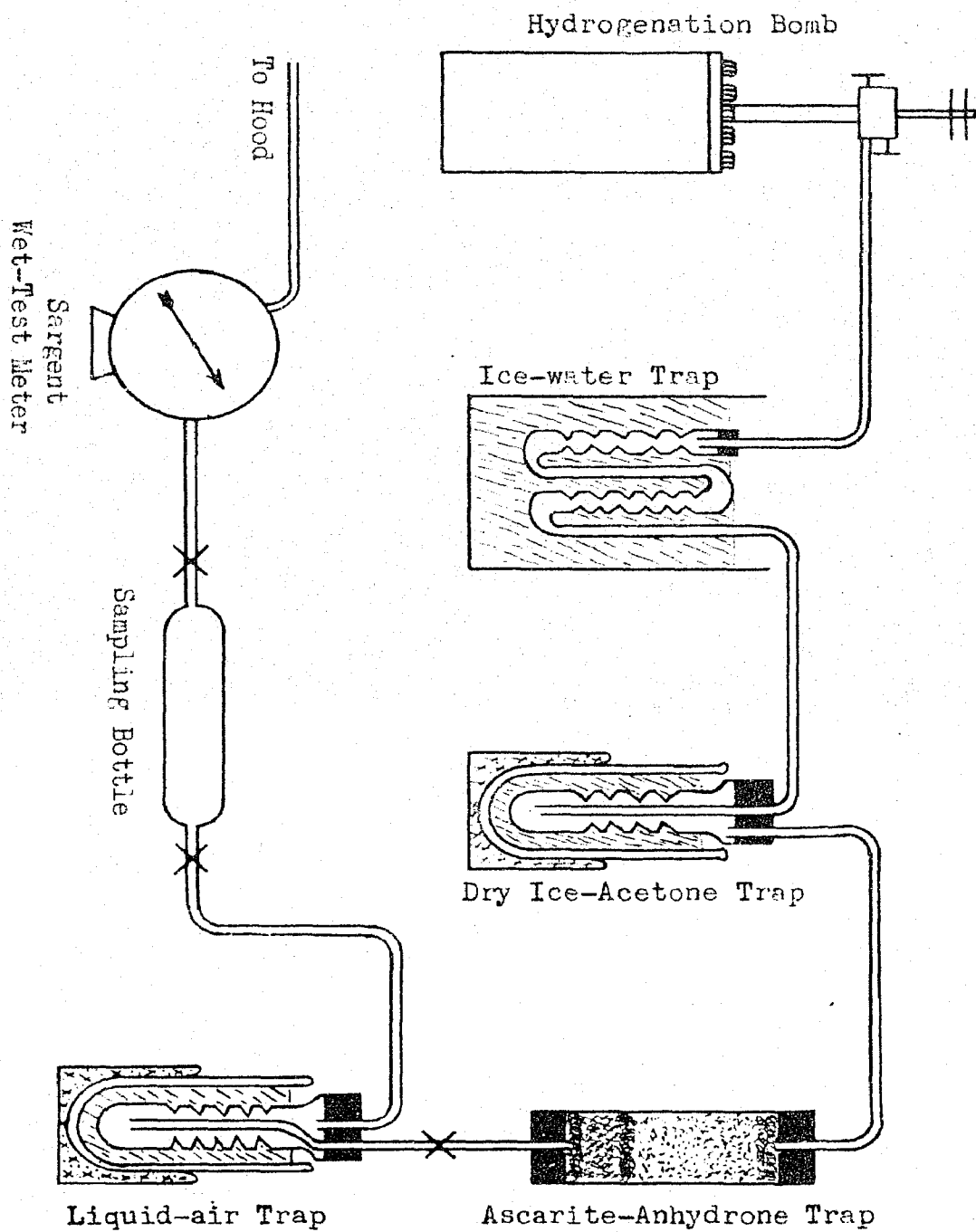
As the reaction gases were removed they had to pass through a series of traps used to separate and isolate the various components. The first trap (No. 1) was immersed in an ice water bath at a temperature of approximately 0°C to condense the higher boiling constituents of the gas and also to cool the remaining portions. The second trap (No. 2) was immersed in a dry-ice acetone bath at a temperature of approximately -70°C used for the same purpose as the first. The third trap (No. 3) was a cylindrical glass tube 9 inches long packed with ascarite and anhydrone used to remove the

carbon dioxide formed during the reaction. The last trap was immersed in liquid air at a temperature of approximately -200°C used to remove the low boiling constituents. After this the non-condensable gases passed through a sampling bottle and a Sargent wet-test meter. The sample of the gas was taken after approximately one half of the gases had been removed from the retort because preliminary experiments indicated that this gave an average representative sample. The Sargent wet-test meter was used to measure the volume. A complete set-up of the absorption train is shown in Fig. 4.

After the gases had been removed from the retort it was closed to the atmosphere and allowed to cool to room temperature. The gas sample that had been collected earlier was analysed using the U. S. Steel Gas Chemists procedure with a Burrell Delux Model H apparatus. The weight of the condensable gases in traps Nos. 1 and 2 was determined and where sufficient quantities were available it was separated into its various constituents by a fractional distillation using a micro-column which will be described later. An attempt was then made to determine the various fractions by obtaining their physical constants.

The weight of carbon dioxide formed during the reaction was obtained by subtracting the weight of CO_2 in the original hydrogen gas from the increase in weight of the ascarite trap.

ABSORPTION TRAIN FOR REACTION GASES



The various low boiling products which had been trapped in the liquid air were identified by their boiling points as determined by a low-pressure distillation using a Podbielniak fractional distillation analysis apparatus, standard precision model J. Although this apparatus is equipped for high as well as low temperature distillations the high could not be used in these experiments because the trap itself acted as the distillation pot rather than the one on the column. Thus the highest boiling material identified with the column was n-butane which has a boiling point of 0°C . Any material remaining in the trap at room temperature was considered as a Podbielniak residue and was separated using the micro-distillation column. Attempts were then made to identify these products by their physical constants.

After the retort had cooled to room temperature as many of the liquid products as possible were removed by suction. However, in the case where the hydrogenation was conducted at 325°C the retort products were in the solid form and had to be removed by scraping. In order to complete the removal of the products, the retort and stirrer were washed with ether. The ether washings and the main bulk of the products in each particular case were then combined, diluted with more ether and filtered to remove any ether insoluble product.

The ethereal solution of retort products was then

extracted with several portions of 5% hydrochloric acid in order to remove any alkaline material. The HCl extract was made basic with 5% sodium hydroxide and extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and stripped of its ether over a steam bath. The result as far as obtaining any products from this ether solution was negative in each case. However, when the HCl extract was made basic there resulted a red brown precipitate which was insoluble in the ether. This product was identified as ferric hydroxide and will be discussed later.

The remaining ethereal solution of retort products after having been extracted with 5% hydrochloric acid was extracted with 5% sodium hydroxide in order to remove any remaining acidic material. The extract solution was made acidic with 5% hydrochloric acid and extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and stripped of its ether over a steam bath. This resulted in the recovery of the acidic compounds most of which were recrystallized and identified.

The remaining ethereal solution of neutral retort products was dried over anhydrous sodium sulphate and stripped of its ether in the usual manner. This resulted in each case in liquid products of various shades of brown and of various viscosities depending upon the temperature and time of hydrogenation. The products of each particular run

were then isolated into their various fractions by a vacuum distillation. The column was packed with 1/8" glass helicies, and was 390 millimeters long with an inside diameter of 9 millimeters and had approximately 12 theoretical plates. The distillation was carried out using a reflux ratio of 4:1, collecting small samples of distillates (approximately 1.5 grams) and measuring their refractive indices at 15°C. Then by plotting the R.I. against the percent of the neutral products the flat portions of the curve indicated an isolated compound.

The various fractions of distillate making up these flat portions of the curve were then combined and purified by a vacuum fractional distillation using a micro column. This column was packed with 3/32 inch glass helices. It is 340 millimeters long, has an inside diameter of 4 millimeters and has approximately 14 theoretical plates. The distillations were preformed using a reflux ratio of approximately 8:1. The column was designed to handle approximately 8 cc and in the purification of the fractions the first 10% and last 20% of the distillate was discarded and only the inbetween 70% was used to obtain the physical constants necessary to identify the compounds.

The physical constants used to identify the majority of the compounds were distillation range, refractive index, specific gravity and an ultimate analysis. The refrac-

tive index was measured with an Abbe Refractometer, the specific gravity with a Fisher-Davidson Gravitometer and the ultimate analysis was determined with a standard combustion furnace. In most cases the constants could not be compared to any values in the literature and it was necessary then to calculate the specific dispersion value according to Thorpe and Larsen's formula (52) in order to help determine the structural formula of the compound.

RESULTS

A general summary of the various results may be found in appendixes I and II. Appendix I included those experiments covering a two hour hydrogenation of the acid at different temperatures and appendix II includes those experiments conducted at 400°C for different lengths of time.

In table I are listed the various experimental conditions used in the hydrogenation of the acid for two hours at different temperatures. The first seven runs are not listed because these were used as preliminary runs in

Table I

Conditions of Hydrogenation for
two hours at different temperatures

Run No.	8	10	12	14	13
Temp. of Hydrogenation - °C	325	370	400	425	450
Initial H ₂ Press. #/in ²	1900	1975	1975	1950	1975
Vol. of H ₂ gas - cu.ft.	5.446	5.701	5.342	5.571	5.642
Pre-heating Period-Min.	80	95	130	130	133
Vol. of Non-Condensable Gas after Hydrogenation cu.ft.	5.335	5.485	5.160	4.890	4.690

order to develop the standard procedures regarding the preparation of the acid, the removal of the gases from the retort and the separation and identification of the retort pro-

ducts. Runs no. 9, 11, 16 and 20 served as check runs for numbers 8, 10, 13 and 12 respectively. Run number 15 was to serve as a check run for no. 14 but difficulty developed and the results had to be discarded. Runs no. 17, 18 and 19 deal with the hydrogenation of the acid at 400°C for one, two and three hours and will be described later.

Figures 5, 6, 7, 8 and 9 present a general summary of the results obtained by hydrogenating the acid for two hours at 325°C, 370°C, 400°C, 425°C and 450°C.

Table II presents the results of the hydrogen consumption as well as the formation of gaseous products during the various reactions. These values are obtained by correcting the amounts actually found for the amounts which are present in the original hydrogen gas.

Table II

Run number	Weight of Hydrogen Consumed and Gaseous Products Formed				
	Grams				
	8	10	12	14	13
H ₂ absorbed	0.40	0.73	1.67	1.99	2.76
CO Formed	0.65	1.66	2.18	2.09	2.47
CO ₂ formed	7.04	8.17	9.17	9.10	8.91
CH ₄ "	1.27	1.50	3.69	2.83	5.83
C ₂ H ₆ "	0.00	0.17	0.47	2.84	2.17
C ₃ H ₈ "	0.02	0.30	3.12	8.02	10.50
i-C ₄ H ₁₀ "	0.00	0.00	1.69	2.55	6.83
n-C ₄ H ₁₀ "	0.00	0.00	0.73	0.61	1.09

Run No. 8

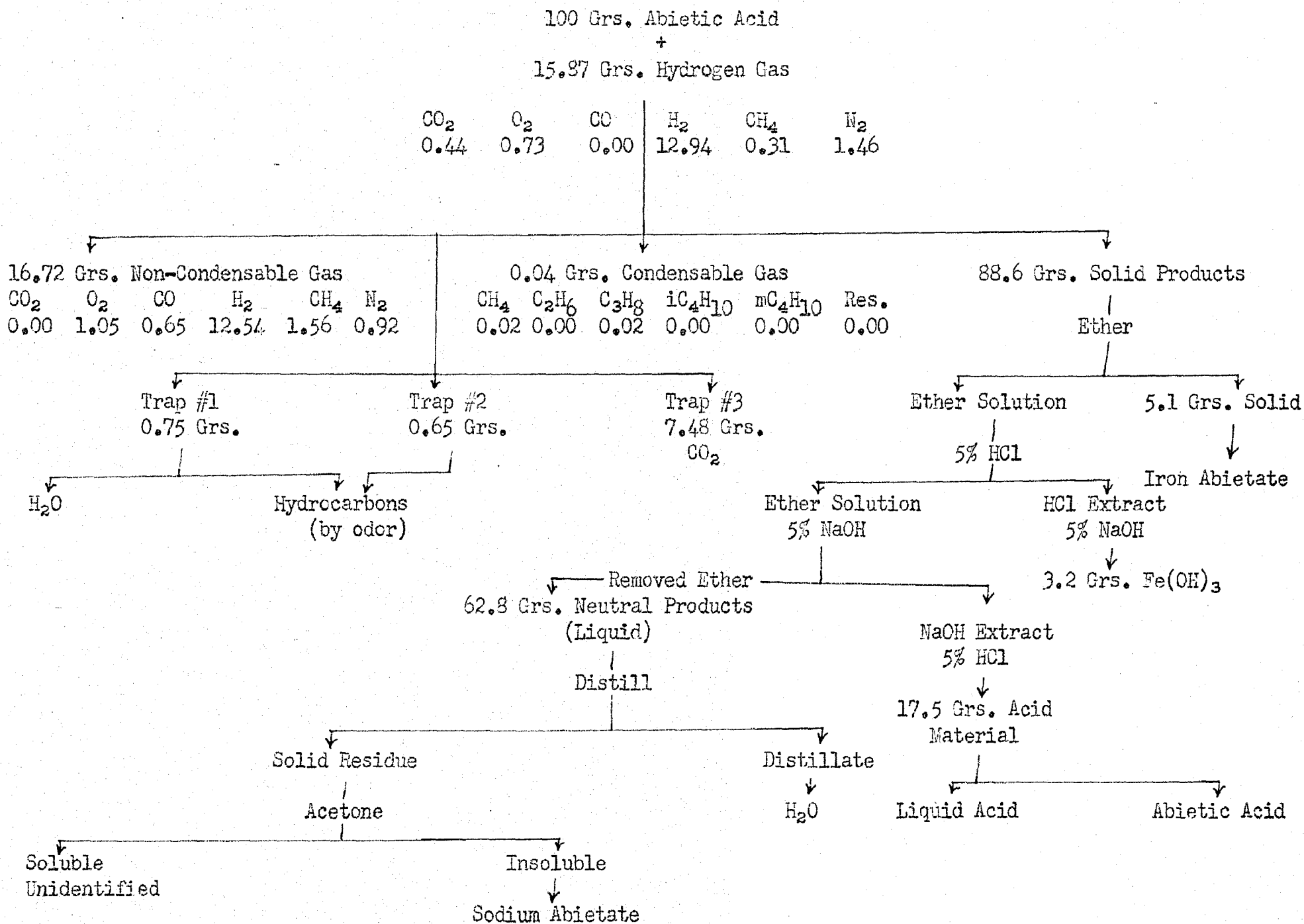


Figure 5

Run No. 10

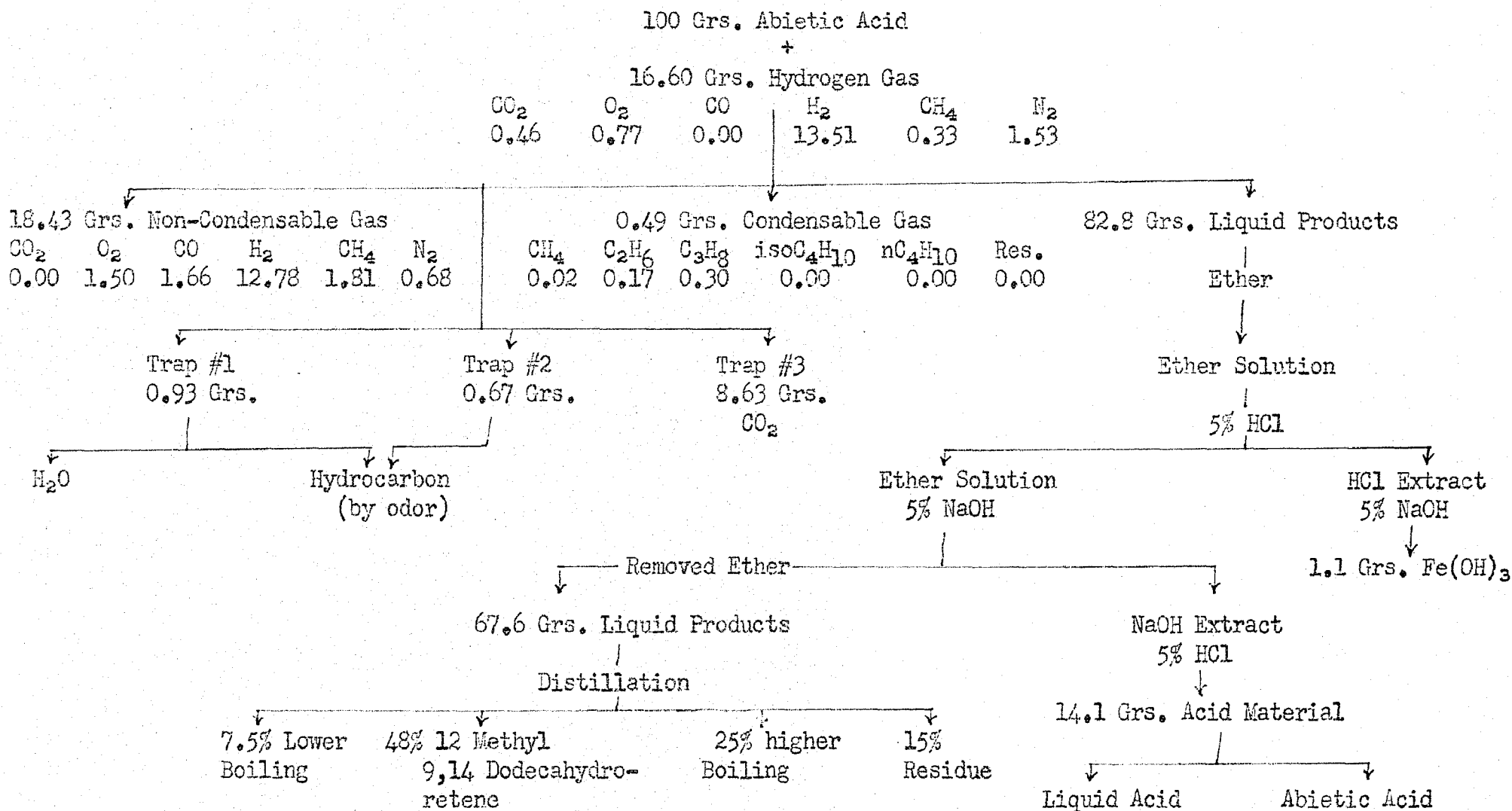


Figure 6

Run No. 12

100 Grs. Abietic Acid

+

16.47 Grs. Hydrogen Gas

CO ₂	O ₂	CO	H ₂	CH ₄	N ₂
0.45	0.76	0.00	13.41	0.33	1.52

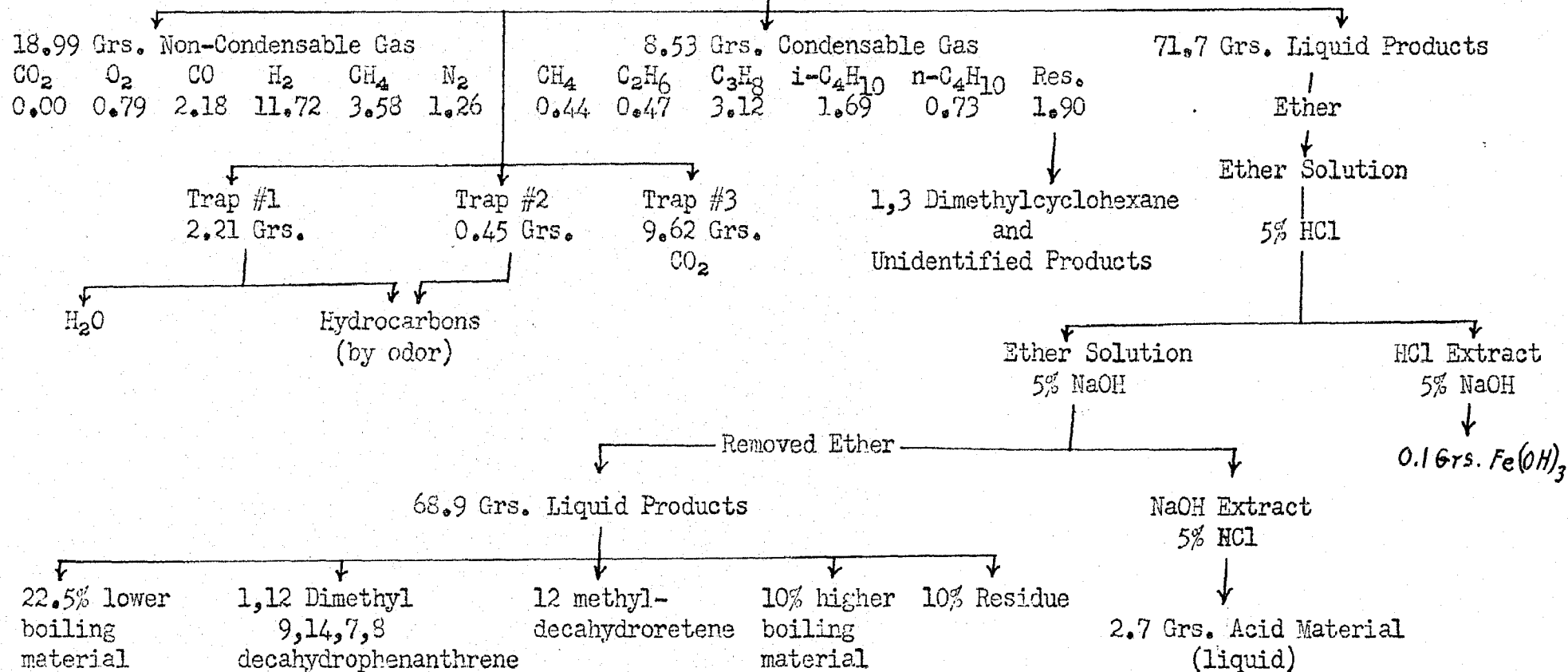


Figure 7

Run No. 14

100 Grs. Abietic Acid

+

16.25 Grs. Hydrogen Gas

CO ₂	O ₂	CO	H ₂	CH ₄	N ₂
0.44	0.75	0.00	13.24	0.32	1.50

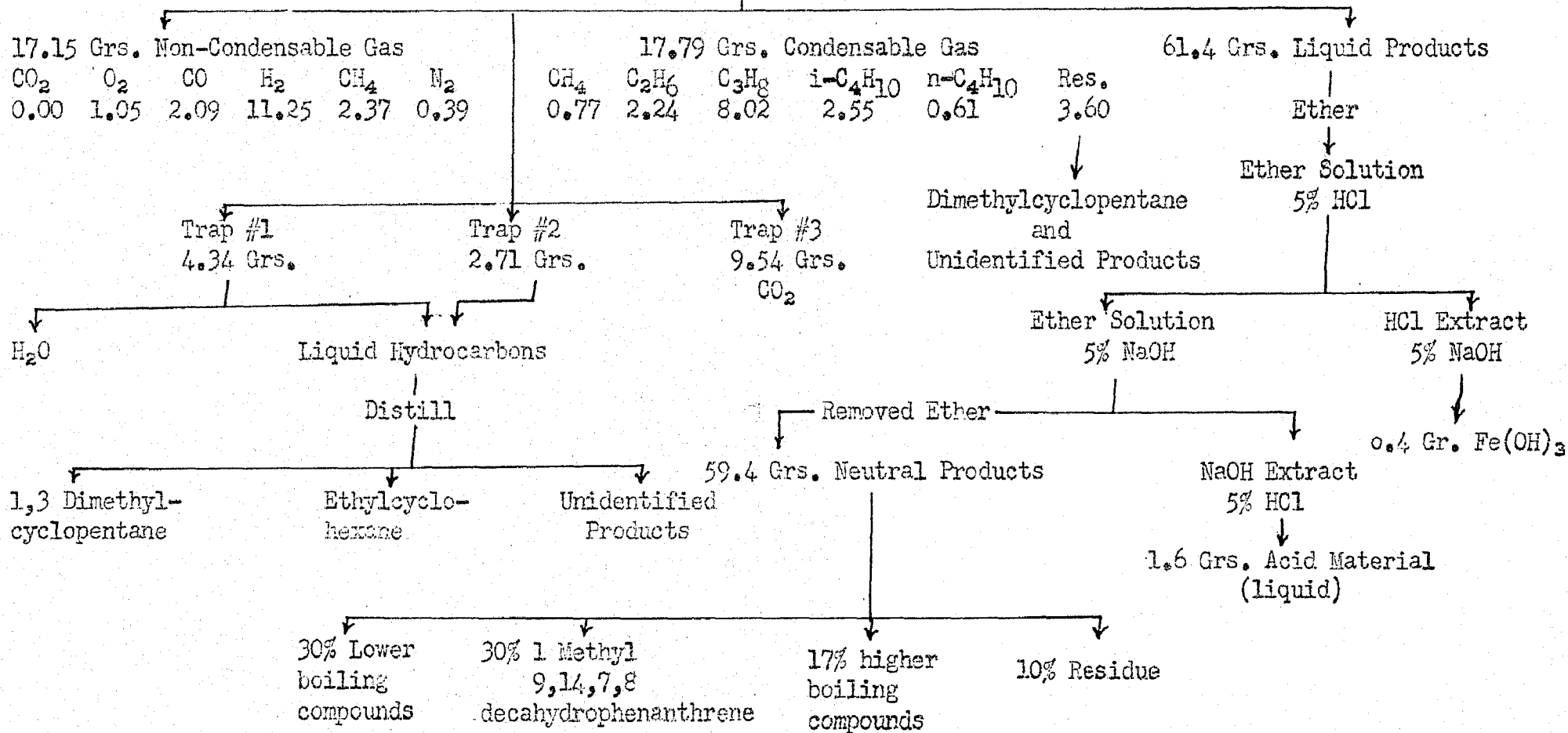


Figure 8

Run No. 13

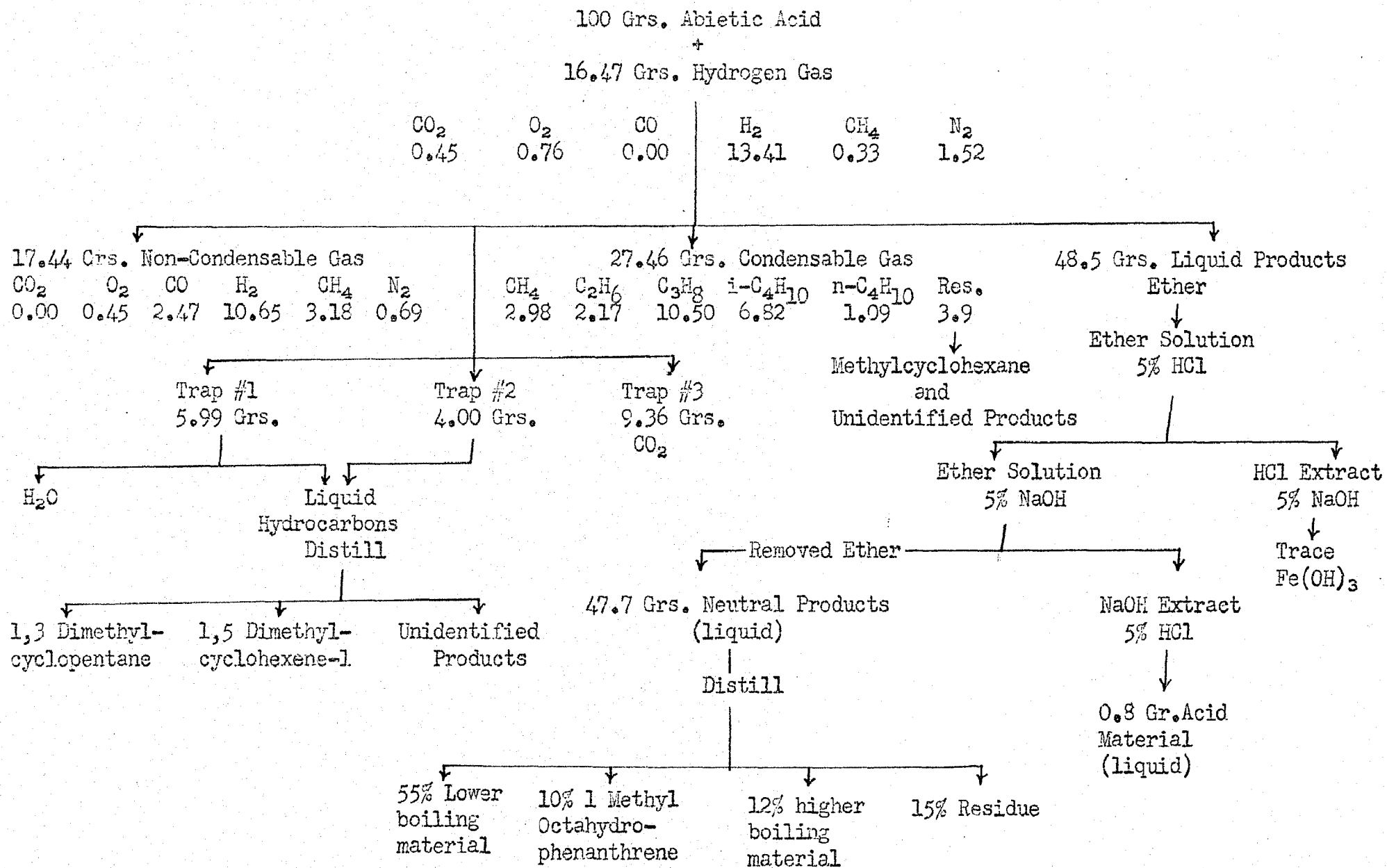


Figure 9

Figures 10, 11, 12 and 13 show the results of the Podbielniak distillations of the condensable gases collected in the liquid air. The curves are obtained by plotting the corrected temperature (to 760 mm Hg pressure) against the accumulative pressure in centimeters of mercury. Since the receiver of the distillates is a calibrated container it is possible to calculate the weights of the various constituents from their partial pressures. From these curves methane is detected by its boiling point of -163°C , ethane at -88°C , propane at -44°C , isobutane at -17°C and n-butane at 0°C . In the first curve propane appears at -35°C but this is due to the fact that there is not enough of the gas to bring the column to equilibrium conditions. The results shown in figure 12 are relatively poor in comparison to the others due to the fact that there is three or four times more material to be distilled than the column is designed to handle. However, based on the previous results shown in figure 11 and later results shown in figure 13 the various components of the gas and their amounts could be determined. From figure 13 it may be seen that the accumulative pressure for the distillation was 315 cm of mercury, in terms of grams of distillate this represents approximately 23 grams. In this particular case sufficient liquid air was available to conduct a slow and as indicated by the curve a rather accurate distillation. The total time required to conduct this distillation was 3 days.

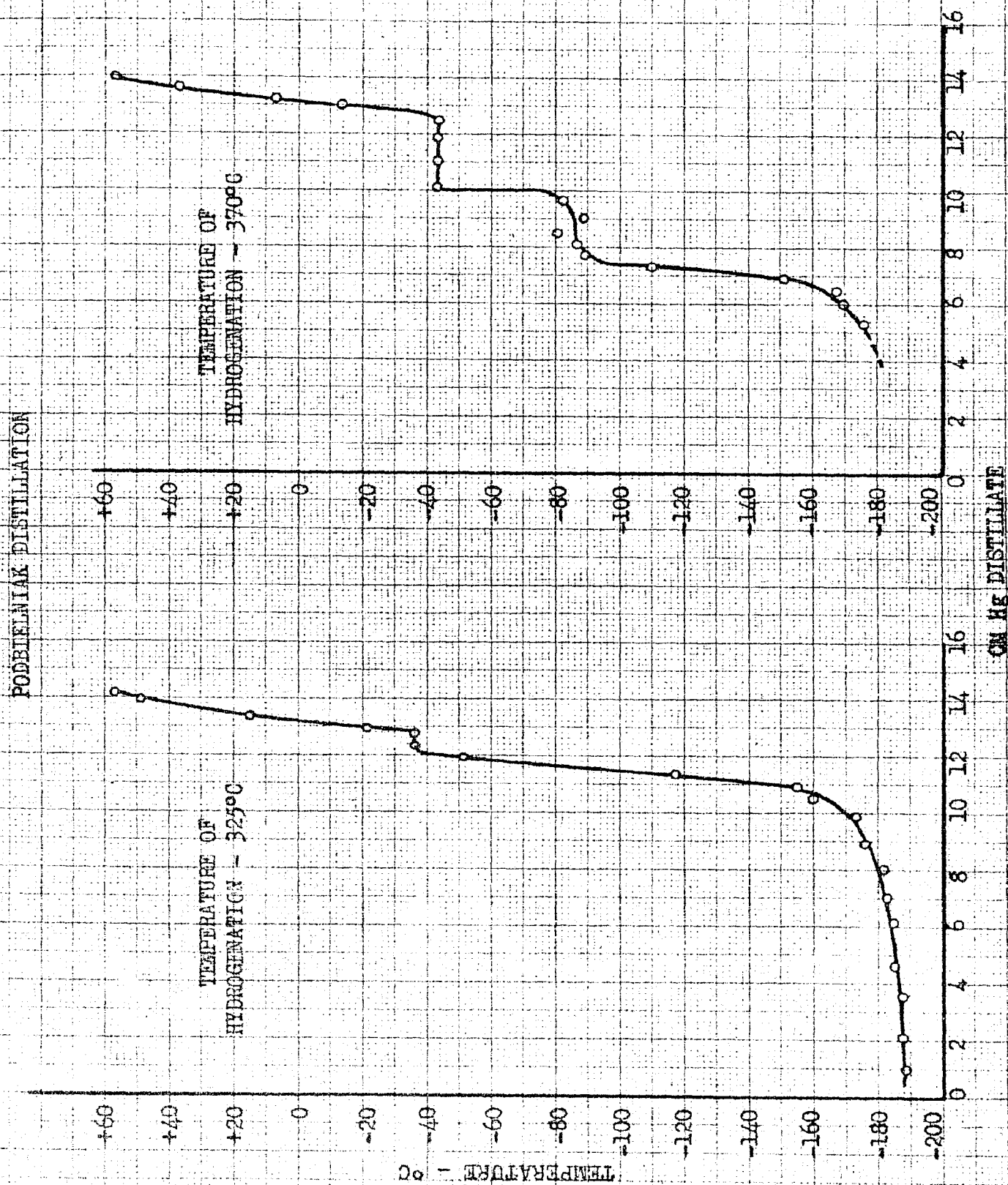
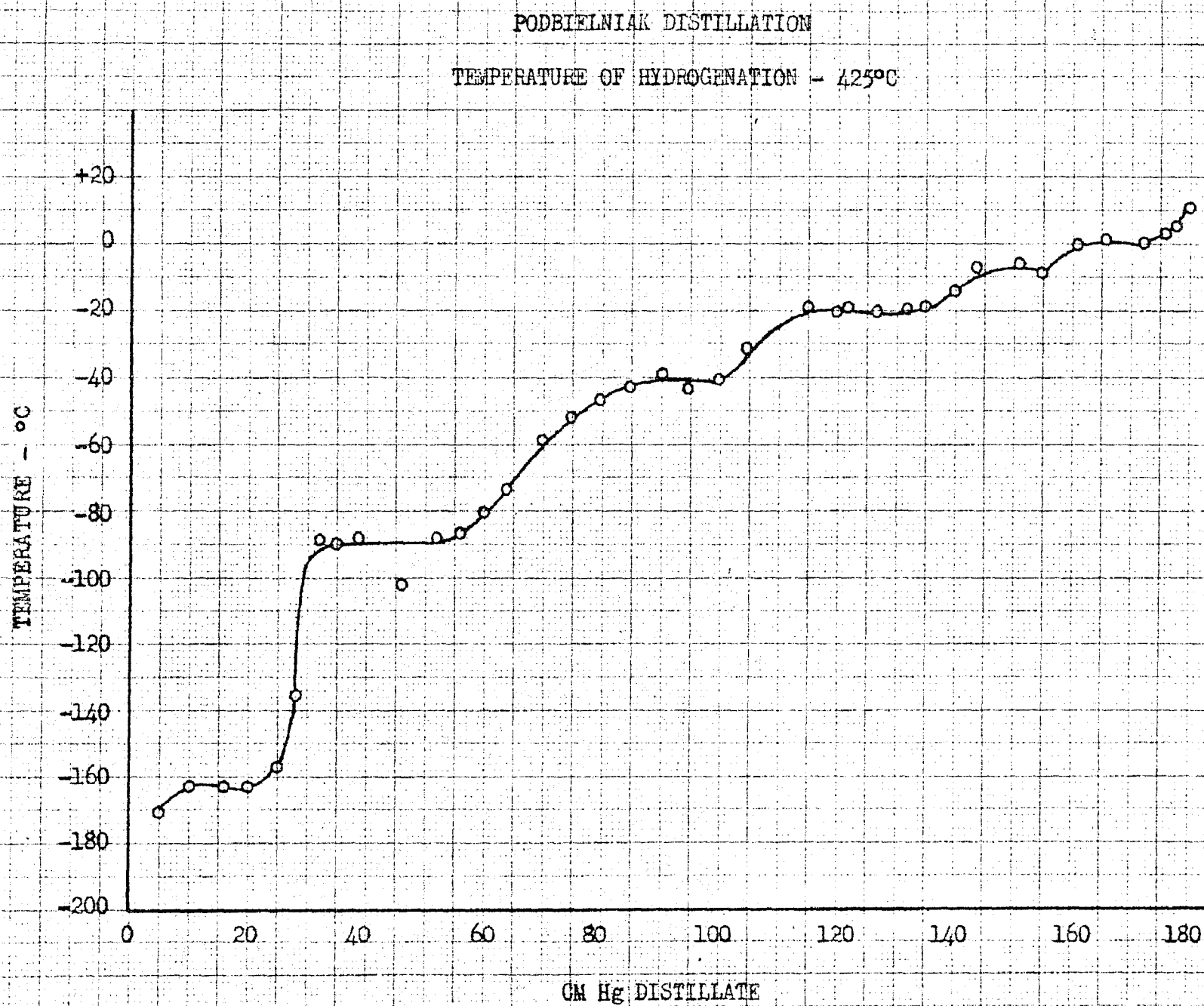


Fig. 10



Fig. 11

Fig. 12



PODBIELNIAK DISTILLATION

TEMPERATURE OF HYDROGENATION - 450°C

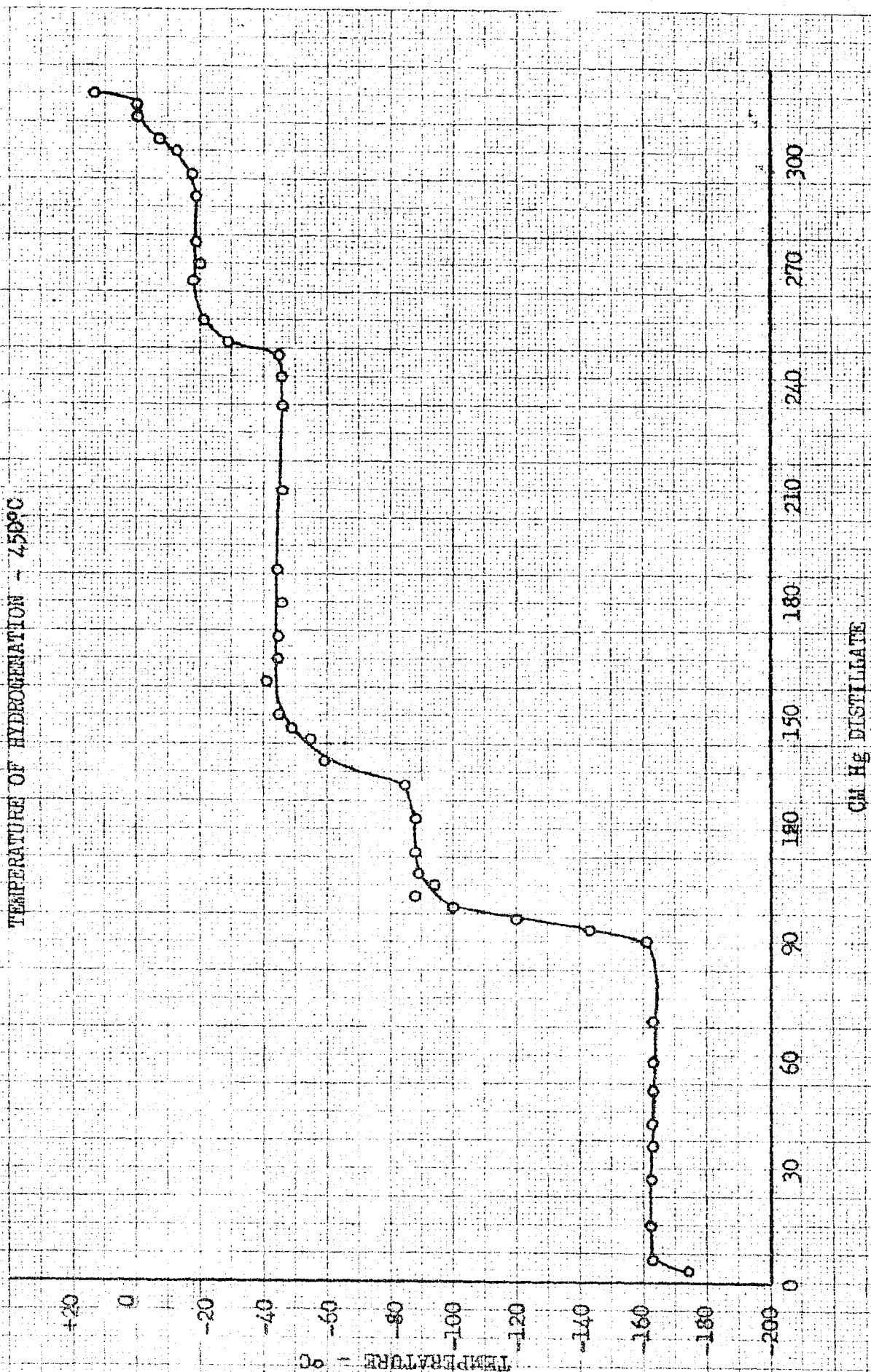


Fig. 13

From the Podbielniak distillations of runs number 12, 14, and 13, where the hydrogenations were conducted at 400°C, 425°C and 450°C, there remained residues of sufficient amounts to warrant further investigation. The residue from run number 12 (400°C) was separated by a micro distillation and yielded products with a refractive index range of 1.3980 to 1.4493 at 20°C. The main portion, however, had a refractive index of 1.4275 at 20°C, a boiling point of 119°C and a density of 0.773 at 20°C. These values agree with those presented by Skita (47) for trans 1, 3 Dimethylcyclohexane. More recent data is given by Margolis (38). Their values are presented below:

	<u>Skita</u>	<u>Margolis</u>
Boiling point	- 119	120.59 to 121.59
Density 20/4	- 0.772	0.7706
Refractive index at 20°C	- 1.4254	1.4262

The Podbielniak residue from the distillation of the products from run number 14 (425°C) amounted to 3.6 grams. However, an attempt was made to analyse this before the micro distillation column and the Fisher-Davidson Gravitometer were available to the laboratory and as a result the physical constants are not too reliable. The residue was first of all stripped of its lighter portion by a distillation over a steam bath. A small fraction distilled at a temperature

less than 40°C and had a refractive index of 1.3691 at 20°C but the main portion did not distill. This portion had a boiling point of 92°C and a refractive index of 1.4155 at 20°C . From these constants it appeared that the substance may be a dimethylcyclopentane. The dimethylcyclopentanes have boiling points ranging from 88 to 92.7°C and refractive indices at 20°C ranging from 1.4093 to 1.4187. The presence of one of the isomers, 1, 3 dimethylcyclopentane, was found in the condensable material of this run and also of run number 13.

The Podbielniak residue from run number 13 (450°C) amounted to 3.9 grams. This was separated by a distillation using the micro column and yielded products with a refractive index ranging from 1.3690 to 1.4426 at 20°C . The main portion had a refractive index at 20°C of 1.4240, a boiling point at 732 mm pressure of 97°C , and a density $20^{\circ}/4^{\circ} = 0.768$. This product is methylcyclohexane which has the following properties according to Egloff (16): R.I. $20^{\circ}/\text{D} = 1.4230$, boiling point at 760 mm = 100.3 and a density $20/4 = 0.769$.

The weight of the condensable material obtained in traps number 1 and 2 from runs number 8, 10 and 12 was not sufficient to warrant further investigation. However, in each case there was obtained two immiscible layers in trap number 1 and the bottom layer was identified as water. The top layer as well as the material in trap number 2 had an

odor which could only be described as a hydrocarbon. There was also obtained in trap number 1 a very small amount of a red brown solid which was identified as iron oxide. In fact this substance was obtained from each hydrogenation and results to be described later will show that it comes from the decomposition of an iron abietate which originally was formed by the action of abietic acid with the iron in the wall of the retort or more likely with the iron in the thermocouple.

The condensable material obtained in traps 1 and 2 of run number 14 (temperature of hydrogenation 425°) was of sufficient amount to be further investigated. The top layer of the material in trap 1 was removed by means of a pipette and added to the material in trap 2. The mixture was then distilled using the micro column and yielded fractions with refractive index ranging from 1.4113 to 1.4520. The main portion had the following physical properties: Boiling point at 731 mm pressure = 128°C , density $20^{\circ}/4^{\circ}$ = 0.783, and refractive index $20^{\circ}/\text{D}$ = 1.4356. From these properties the substance was identified as ethyl cyclohexane which is reported by Levina (34) to have a boiling point at 750 mm pressure of 130°C , a density $20/4$ = 0.785, and a refractive index $20/\text{D}$ = 1.434.

It was reported above that the first fraction to be distilled from the products trapped in ice water and dry ice acetone baths from run number 14 had a refractive index $20^{\circ}/\text{D}$ =

1.4113. It was also discovered that the first fraction of distillate from the same condensable material from run number 13 had a refractive index $20^{\circ}/D = 1.4110$. These two fractions were believed to be the same compound so they were combined in order to have enough to determine the other physical properties. The boiling point of the fraction varied from $90-91^{\circ}\text{C}$ at 729 mm pressure and the density was found to be 0.743. From these constants the compound may be identified as 1, 3 dimethylcyclopentane. The constants reported in the literature for this compound by Evans (17) are: b.p. at 760 = 90.5 , density $20/4 = 0.7463$ and R.I. $20/D = 1.4096$.

The remainder of the condensable material obtained in traps 1 and 2 from run number 13 distilled with fractions of a refractive index range up to 1.4630. The main portion had the following physical properties: b.p. at 732 = 128°C , density $20/4 = 0.792$ and R.I. $20/D = 1.4430$. This is believed to be 1,5 dimethylcyclohexene -1 which is reported by Knoevenagel (29) to have the following properties: b.p. $124-5^{\circ}\text{C}$, density = 0.8005 at 18°C and R.I. $20/D = 1.4430$.

On examining the products remaining in the retort after the gases had been removed there was found one which appeared to be ether insoluble. This product was obtained in run number 8 where the hydrogenation had been conducted at 325°C . Closer examination of the product revealed that it was very slightly soluble in ether but it is listed in

the appendix as an ether insoluble product. It was a light grey amorphous solid with a characteristic undescribable odor and a decomposition range of 230-250°C. On ignition it decomposed into a black solid which bursts into a bright flame and leaves a dark red residue. This residue was tested and gave positive results with KCNS and $K_4Fe(CN)_6$ thus indicating iron. The substance reacted with 5% NaOH to form a red brown precipitate of ferric hydroxide. After the hydroxide had been removed by filtration the filtrate was made acidic with 5% HCl. This resulted in a white precipitate which was extracted with ether, recovered from the ether solution and recrystallized. The recrystallized material had a melting point range of 156-8°C, the same as the original acid and there was no change in a mixed melting point with freshly prepared abietic acid. From this data it may be concluded that the so-called ether insoluble material is an iron salt of abietic acid. It is believed that the iron is present in the ferrous state because decomposition with boiling water results in a positive test for the ferrous as well as the ferric ion.

Upon extracting the ether solution of retort products from each run with 5% hydrochloric acid and making the acid extract basic with 5% sodium hydroxide there resulted a red brown precipitate which was insoluble in ether. This precipitate was identified as ferric hydroxide by its positive tests with KCNS and $K_4Fe(CN)_6$. It was separated by filtra-

tion, dried and weighed. The amount obtained depended upon the temperature of hydrogenation: 3.2 grams when the temperature was 325°C, 1.1 grams at 370°C, 0.1 grams at 400°C, 0.4 grams at 425°C and only a trace at 450°C. With the exception of the 0.1 gram at 400°C, which is probably an error, the amounts appear to be in direct relation to the amount of acid material remaining after hydrogenation. From this as well as the previous identification of an iron abietate it seems likely that the iron obtained by the HCl extraction came from iron abietate which was soluble in ether. In other words that the HCl reacted with the abietate to form ferric chloride and abietic acid and that the ferric chloride was extracted in the aqueous solution and the abietic acid remained in the ether solution.

After the ether solutions of retort products had been extracted with 5% hydrochloric acid they were extracted with 5% sodium hydroxide. The NaOH extracts were then acidified with 5% HCl, and extracted with ether. The ether solutions were dried over anhydrous sodium sulphate and stripped of their ether over a steam bath. The result in each case was a liquid acidic material of the amount shown below:

Temperature of Hydrogenation	Grams of Acidic Material
325°C	17.5
370°C	14.1
400°C	2.7
425°C	1.6
450°C	0.8

However, in the case of the first three mentioned a white crystalline substance was formed on standing over night. These crystals represented approximately 90% of the total amount present. They were separated by filtration, recrystallized from 90% alcohol and found to have a melting point range of $156 - 8^{\circ}\text{C}$ the same as the original abietic acid. A mixed melting point with the freshly prepared original acid gave the same value.

The identity of the remaining liquid acidic material was not definitely established because of its small quantity, but it had a refractive index at $20^{\circ}\text{C} = 1.524$ and an ultimate analysis of $80.76 - 80.65\% \text{C}$, $10.53 - 10.80\% \text{H}_2$ and $8.71 - 8.55\% \text{O}_2$. It also gave a negative test for unsaturation. From this it appears likely that the acid may be tetrahydro-abietic acid about which there is very little data in the literature and the literature which is available is rather confusing.

The main products of all the runs were those which remained in the ether solution during the extraction with 5% hydrochloric acid and 5% sodium hydroxide. These were called the neutral products.

A vacuum distillation of the neutral products from run no. 8 (325°C) yielded a water distillate and wax-like residue which would not distill. It is quite likely that the water was obtained during the extraction of the ether solution

with aqueous acid and alkali. After conducting several preliminary experiments with the wax-like residue it was discovered that a portion of it could be separated by solution in hot acetone. This portion recrystallized when the acetone solution was cooled in the refrigerator but great difficulty was encountered in attempting to separate the crystals by filtration because they turned into a wet sticky mass on the filter paper. This was probably due to its absorption of moisture from the air. An attempt was then made to filter the crystals in a desiccator over phosphoric anhydride. This was successful but even after drying them in a vacuum at 65°C it was impossible to determine their melting point because of their transformation into the "sticky" mass.

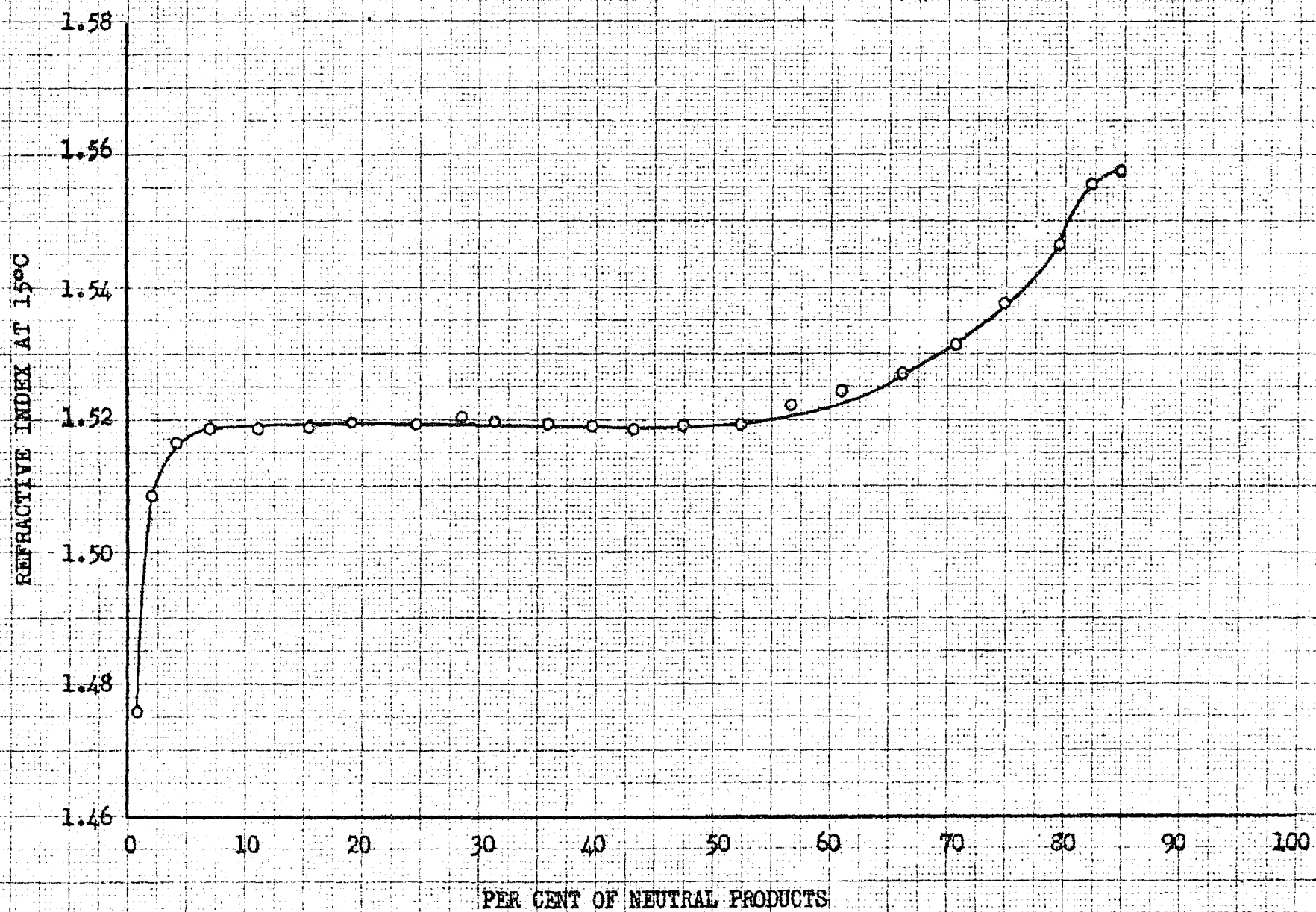
The residue from the acetone extraction was a light brown powder-like solid with no particular odor. On ignition it would decompose, catch fire, burn with a bright flame but without much smoke and leave a light residue which was identified as sodium. The material did not have a definite decomposition temperature but would start to turn brown at about 170°C and keep getting darker until it was black at 225°C . It was completely soluble in water and on addition of 5% HCl would yield a heavy white precipitate. The precipitate was recovered by filtration, recrystallized from 90% alcohol and found to have a melting point range of $156-8^{\circ}\text{C}$. A mixed melting point with the original acid definitely identified it as

abietic acid and thus the acetone insoluble material may be identified as sodium abietate.

Figure 14 shows the result of the vacuum distillation of neutral products from run number 10 (370°C). From the curve it may be seen that a large percentage (approximately 48% or roughly 32 grams) of the products is a single compound with a refractive index of around 1.519 at 15°C. Approximately 7½% of the total neutral products have a lower boiling range than this product and approximately 25% of the products have a higher boiling range. There was also a residue from the distillation of approximately 15%. This residue may be described as a light brown viscous liquid which seemed to polymerize to a solid on standing in the laboratory. This same type of residue resulted from each of the vacuum distillations of neutral products.

The main product from the run was purified by a microdistillation and found to have a distillation range of 139 to 143°C at 4 mm pressure. It was a colorless liquid with an undescribable organic odor. It was found to be an unsaturated compound by its positive reaction with bromine in carbontetrachloride and with potassium permanganate. The physical constants for the compound as well as the ultimate analysis are listed below and compared to the theoretical values for 12 methyl Δ 9,14 dodecahydrotetene.

VACUUM DISTILLATION
OF NEUTRAL BOMB PRODUCTS
FROM RUN No. 10



Physical Constants	Unknown	12 methyl Δ 9,14 dodecahydroretene
Density 20/4	0.943	
R.I. 20/D	1.5165	
% C	87.68 87.73	87.61
% H	12.14 12.12	12.39
Sp. Disp.	107.1	107.9

It is assumed in all the calculations of specific dispersion that the double bonds present in the original abietic acid are in the 9, 14, 7, 8 positions. From the close agreement of the specific dispersion values it appears that the bond in the 7,8 position is probably the one to be saturated, although the value for the same isomer assuming the bond in the 9,14 position to be saturated is 108.2. Both values are therefore within the limits of experimental error so that it cannot be definitely established as to which bond has been saturated.

The result of the vacuum distillation of neutral products from run number 12 is shown in figure 15. From the figure it may be seen that there are two possible products which could be isolated. These two account for approximately 45% of the neutral products. It may also be seen that there is approximately 22.5% lower boiling and about 12% higher boiling compounds. The residue in this case amounted to approximately 10% and the % loss was quite high for this distillation.

VACUUM DISTILLATION
OF NEUTRAL BOMB PRODUCTS
FROM RUN NO. 12

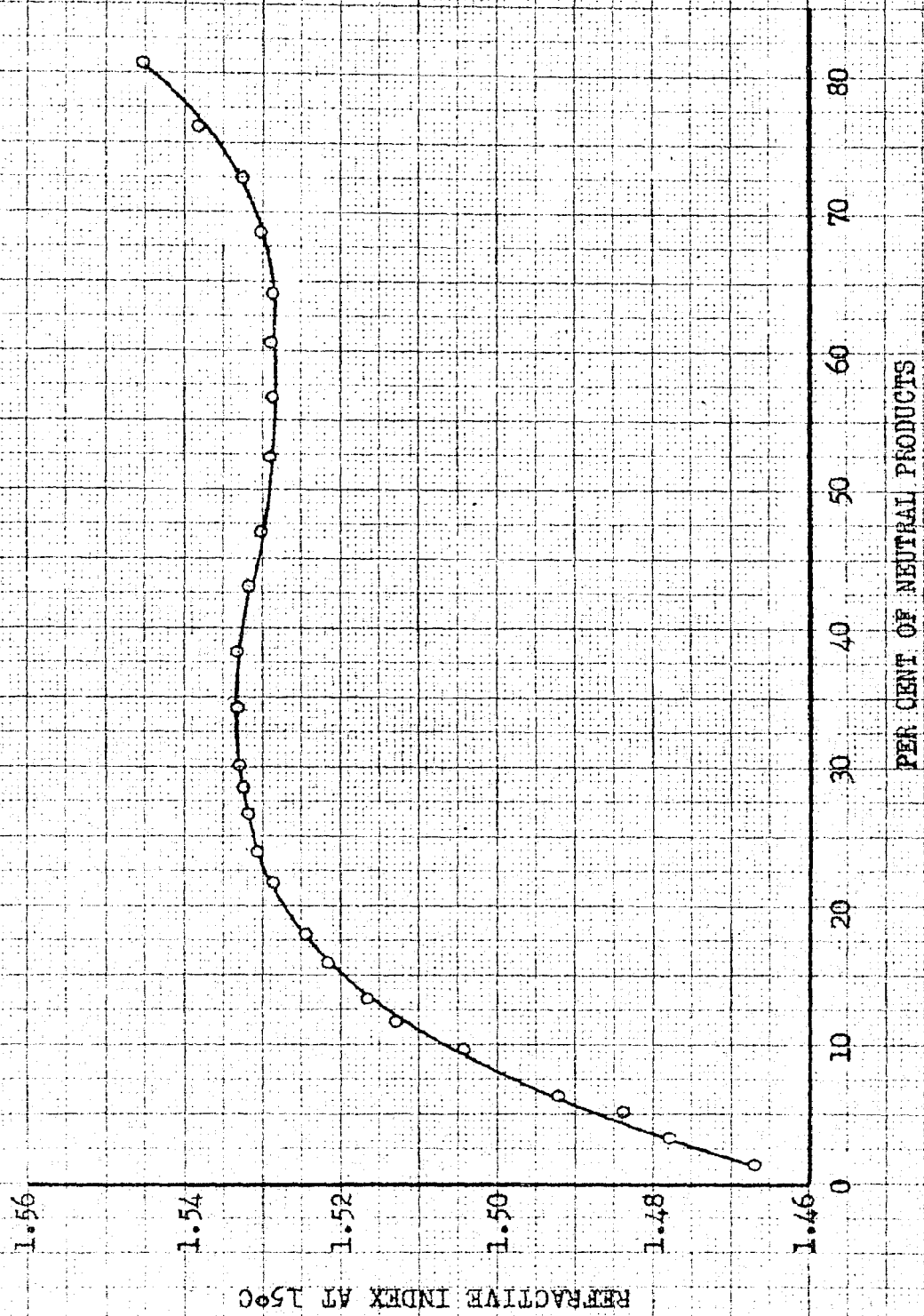


Fig. 15

The first compound to be isolated had a lower boiling point and a higher refractive index than the second. It was purified in the usual manner and found to have a distillation range of 122 to 125°C at 4 mm pressure. It may be described as a colorless oil with a characteristic undescribable odor. It gave positive tests with bromine in carbon tetrachloride and with potassium permanganate indicating unsaturation. The physical constants as well as the ultimate analysis of the compound are listed below together with the theoretical values for 1,12 Dimethyl Δ 9,14,7,8 decahydrophenanthrene. In the location of the double bonds it has been assumed that they are the same as those present in the original abietic acid, however, it is definitely established by the high specific dispersion that the bonds are in conjugated positions.

Physical Constants	Unknown	1,12 Dimethyl Δ 9,14,7,8 decahydrophenanthrene
Density 20/4	0.946	
R.I. 20/D	1.5312	
% C	88.68 88.67	88.81
% H	11.13 11.15	11.19
Sp. Disp.	144.0	144.6

The second compound, the one with the higher boiling point and lower refractive index, is a very pale green oil with a characteristic but undescribable odor. This compound also indicated unsaturation with the tests mentioned above but with

greater difficulty. In this case the permanganate test required mild heating with hot water before positive results were obtained. Its distillation range on purification was 143 to 146°C at 5½ mm pressure. Its physical properties and ultimate analysis are listed below with the theoretical and calculated values for 12 methyldecahydrotetene:

Physical Constants	Unknown	12 methyldecahydrotetene
Density 20/4	0.943	
R.I. 20/D	1.5250	
% C	88.13 88.19	88.29
% H	11.78 11.73	11.71
Sp. Disp.	137.4	137.4

The location of the double bonds have not been definitely established. However, for the specific dispersion value listed above (137.4) the bonds are in conjugate positions but not in the 7,8 position for if this were the case the calculated specific dispersion would be 140.5. This indicates that if one of the double bonds in the original acid (9,14; 7,8), was saturated as indicated in the previous run it was the one in the 7,8 position and if dehydrogenation occurred it would take place in either the 10,11; 12,13; or 5,13 positions as any of these combinations with the 9,14 bond would satisfy the calculated specific dispersion value. If, however, saturation

of one of the bonds in the original structure did not take place the structural formula listed in figure 2 is not correct and would probably have to be changed so that the double bonds would be in the 9,14 and 5,13 positions.

Figure 18 shows the results of the vacuum distillation of neutral products from run number 14 (425°C). In this case there was only one product identified even though there were two breaks in the curve because the second product only amounted to roughly 5% of the total. The main product amounted to roughly 30% of the neutral products and there were 30% lower boiling and 27% higher boiling compounds as well as about 10% of residue.

The main fraction was purified in the usual manner and found to have a distillation range of 118 to 120°C at 3 mm pressure. It is a colorless oil with an odor similar to kerosene. Both tests mentioned above for unsaturation are positive. The comparison of the compound with the theoretical values for 1 methyl Δ 9,14,7,8 decahydrophenanthrene are listed below:

Physical Constants	Unknown	1 Methyl Δ 9, 14, 7, 8 decahydrophenanthrene
Density 20/4	0.946	
R.I. 20/D	1.5329	
% C	88.92 88.93	89.03
% H	10.91 10.91	10.97
Sp. Disp.	148.2	147.8

VACUUM DISTILLATION
OF NEUTRAL BOMB PRODUCTS
FROM RUN No. 14

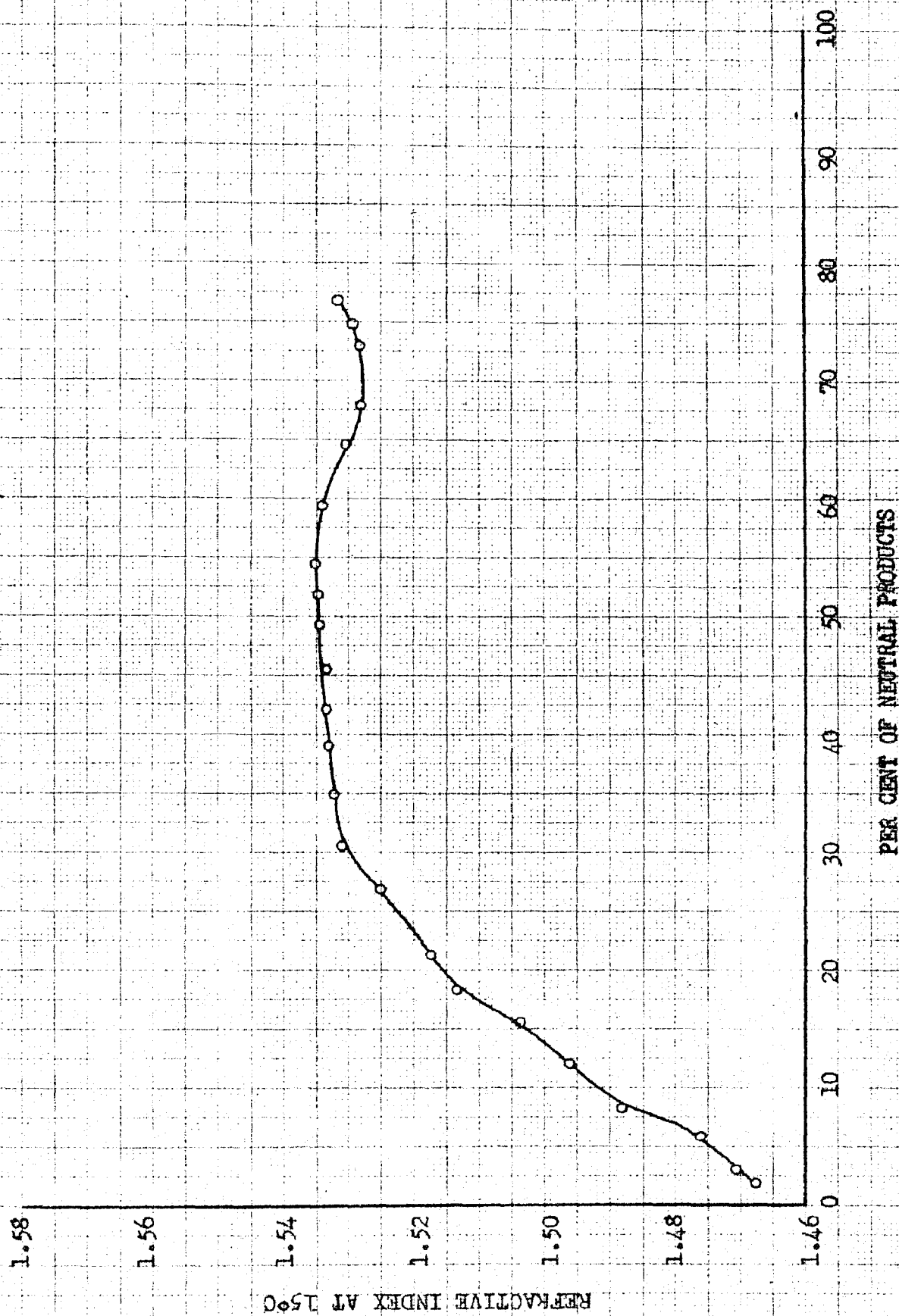


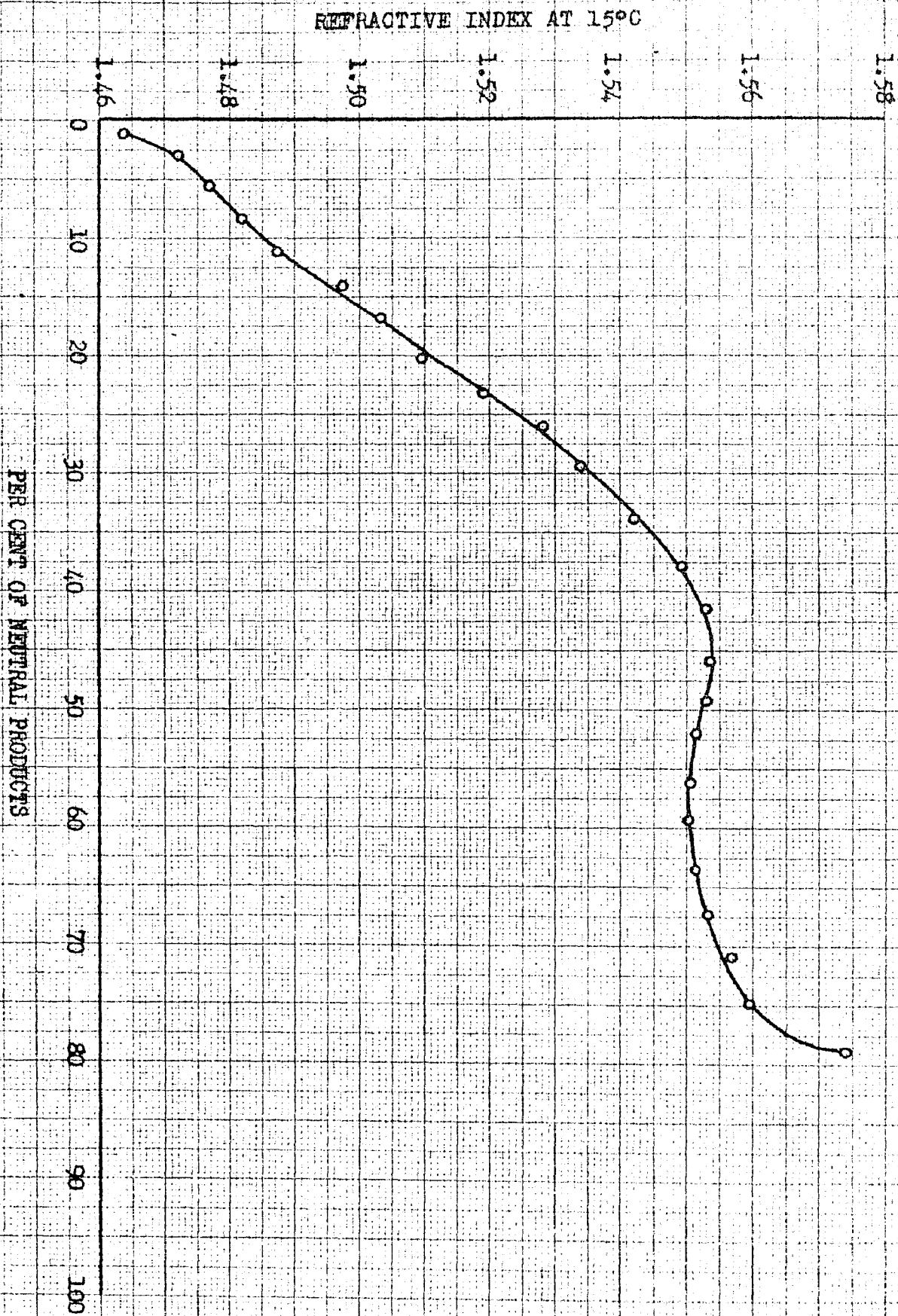
Fig. 16

It is also quite possible that the second product to be isolated in this run (14) with the higher boiling point and lower refractive index is 12 methyldecahydroretene because the refractive index at 15°C (figure 16) is within the experimental range of the second product from run number 12 (figure 15). However, the actual purification and determination of physical properties has not been conducted for lack of sufficient amount of the material.

The result of the vacuum distillation of neutral products from run number 13 (450°C) is shown in figure 17. From the curve it may be seen that only one product could be isolated. This represented roughly 10% of the neutral products while the lower boiling fractions amounted to approximately 55%, the higher boiling fractions 12% and the residue 15%.

The isolated fraction was purified in the usual manner and found to have a distillation range of 112 - 116°C at 4 mm pressure. It is a colorless oil with an odor similar to kerosene. Its physical properties and calculated specific dispersion value are listed below and compared to 1 methyl-octahydrophenanthrene.

Physical Constants	Unknown	1 methyl-octahydrophenanthrene
Density 20/4	0.951	
R.I. 20/D	1.5476	
% C	89.64 89.73	89.92
% H	10.06 10.11	10.08
Sp. Disp.	179.9	172.8



Of the various isomers which are possible for an octahydrophenanthrene it is believed that the one obtained in this case is the 1 methyl Δ 9,14; 5,13; 7,8 octahydrophenanthrene. This possibility has a calculated specific dispersion of 172.8. Other possibilities and their calculated specific dispersion values are listed below:

Possibilities	Specific Dispersion
Δ 9,14,7,8,10,11	185.3
Δ 9,14,7,8,12,13	185.3
Δ 9,14,10,11,12,13	149.9

Although the first two values agree a little closer to the experimental 179.9 value these have been eliminated because the purified compound may contain a trace of a higher boiling, higher refractive index compound which was necessary in this particular case in order to obtain a sufficient amount for the physical tests. This being true the experimental specific dispersion value would be slightly higher than the theoretical value which is the case.

In table III are listed the various experimental conditions used in the hydrogenation of the acid for different lengths of time at 400°C.

Table III

50

Conditions for Hydrogenating Acid at 400°C for different lengths of time

Run Number	17	18	18	19	19	19
Time of Hydrogenation	1 hr.	1st. hr.	2nd. hr.	1st. hr.	2nd. hr.	3rd. hr.
H ₂ Press. #/in ²	1925	1940	1940	1925	1920	1910
Vol. H ₂ Gas Cu. Ft.	5.530	5.565	5.520	5.500	5.530	5.460
Pre-heating period - Min.	85	92	87	88	90	90
Vol. of Non-Condensable Gas after hydrogenation cu. ft.	5.465	5.520	5.530	5.425	5.511	5.520

Table IV presents the results of the hydrogen consumption as well as the amounts of gaseous products formed during the hydrogenations for one, two and three hours at 400°C. These results are compared to the ones obtained by hydrogenating the acid for two hours at 400°C.

Table IV

Weight of Hydrogen Consumed and Gaseous Products Formed

Run No.	12	17	18	19
Time of Hydrogenation	2 hrs. Continuous	1 hour	2nd. 1 hour period	3rd. 1 hour period
H ₂ absorbed	1.67	0.48	0.00	-0.02
CO Formed	2.18	2.22	0.56	0.19
CO ₂ "	9.17	8.90	0.03	-0.22
CH ₄ "	3.69	2.00	1.03	1.03
C ₂ H ₆ "	0.47	0.00	0.00	0.00
C ₃ H ₈ "	3.12	0.98	0.53	0.37
Higher H-C	2.42	0.00	0.00	0.00

Figure 18 shows the result of the Podbielniak distillations of the products trapped in liquid air. The first curve represents the products after the first hour of hydrogenation. From this curve methane and propane are detected with possibly a trace of n-butane. The remaining two curves represent the gases after the second and third one hour periods of hydrogenation. From these curves only propane may be detected.

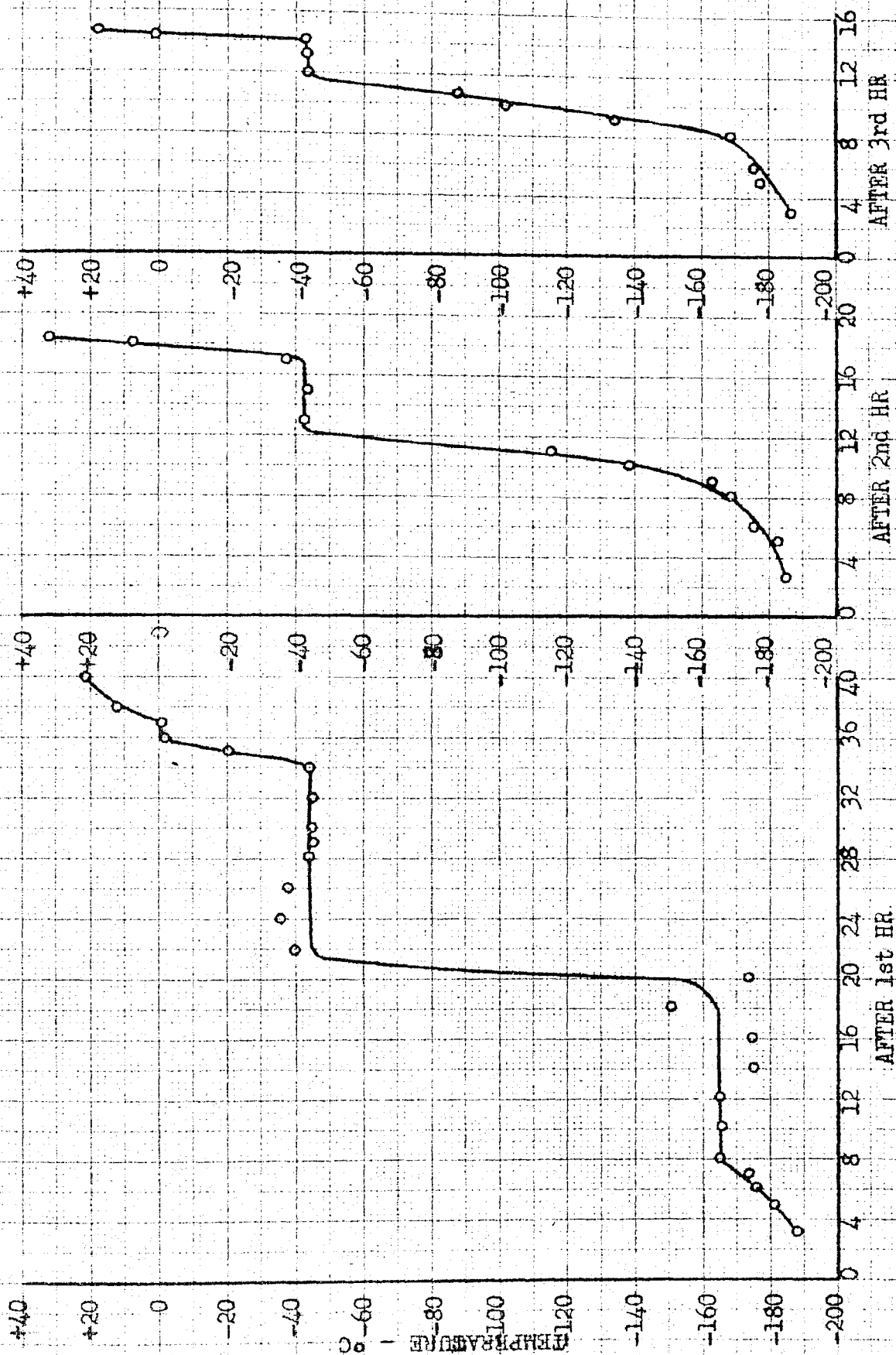
The residues from all of the Podbielniak distillations (Runs 17, 18 and 19) were combined and distilled using the micro distillation column. These residues amounted to 3.6 grams and yielded distillates with refractive indices at 20°C ranging from 1.3781 to 1.4598 but there was not a sufficient amount of any one product to be identified.

The amount of material trapped in the ice water and dry ice acetone traps was not large enough to warrant further investigation but again the two layers were obtained in trap number 1 and the bottom was identified as water.

On extracting the retort products obtained from hydrogenating the acid for 1, 2 and 3 hours with 5% HCl and then making the extract basic with 5% NaOH there was obtained 0.3 grams after the first hour and only a trace after the second and third of the red brown precipitate discussed above. The acidic compounds remaining in the retort amounted to 3.4 grams after the first hour, 0.8 grams after the second

PODBIELNIAK DISTILLATION

TEMPERATURE OF HYDROGENATION - 400°C



CM Hg DISTILLATE

and 0.8 grams after the third. These values may be compared to the 2.7 grams which remained after the hydrogenation at 400°C for 3 hours.

Figures 19, 20 and 21 show the results of the vacuum distillations of neutral products remaining in the retort after hydrogenating the acid for one, two and three hours respectively at 400°C. From the curves it may be seen that in each case two products may be isolated which represent approximately 50% of the neutral products. The lower boiling material amounted to roughly 10%, and the higher boiling to roughly 36%. There is about 10% residue in each case and about 4% loss.

After the isolated compounds had been purified in the usual manner and their physical constants determined, the exact structures of the compounds could not be established because of the disagreement of their specific dispersions with all of the theoretical possibilities. In table V are presented the results of the physical constants and ultimate analyses of four of the isolated compounds which have been purified.

VACUUM DISTILLATION
OF NEUTRAL BOMB PRODUCTS
FROM RUN No. 17

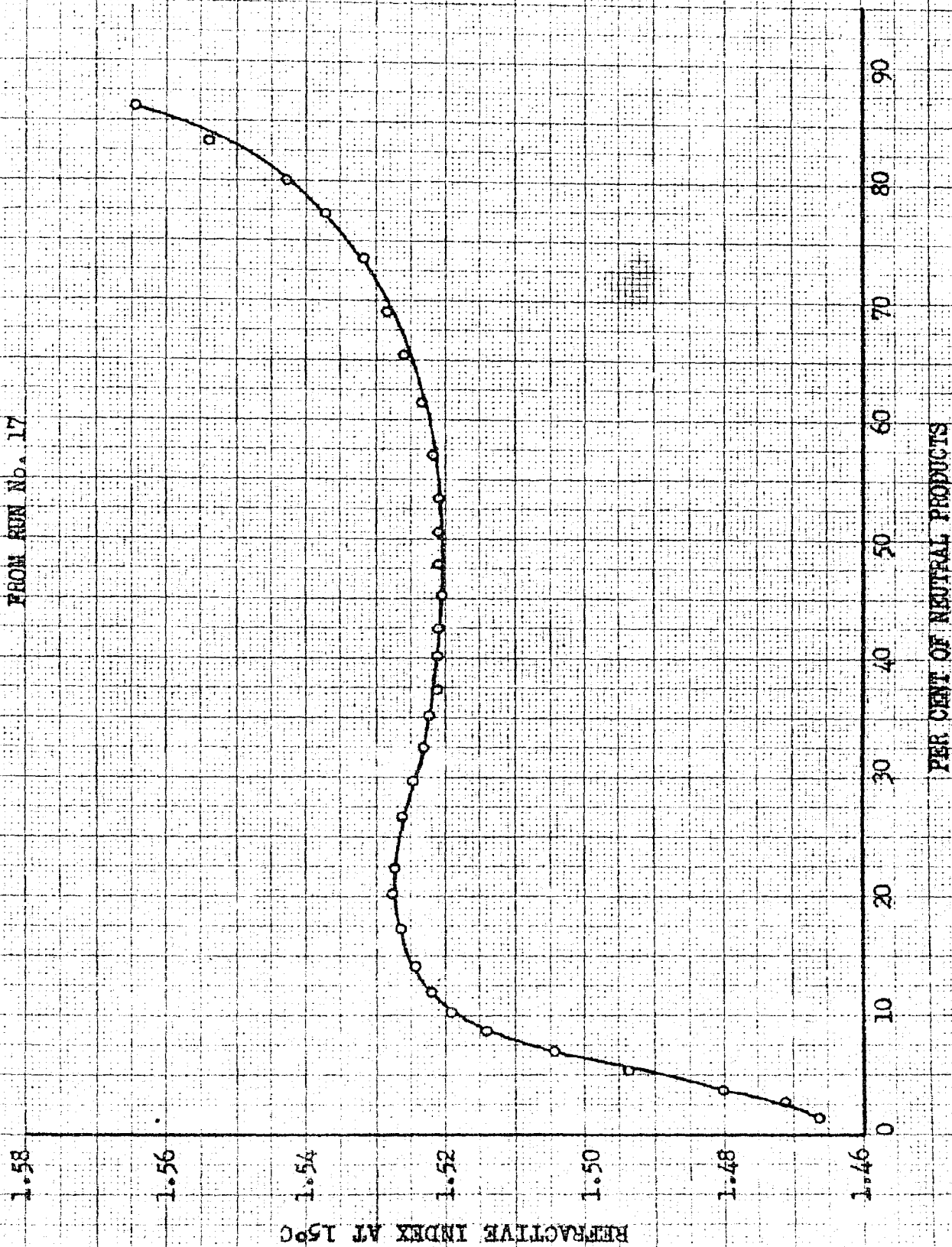
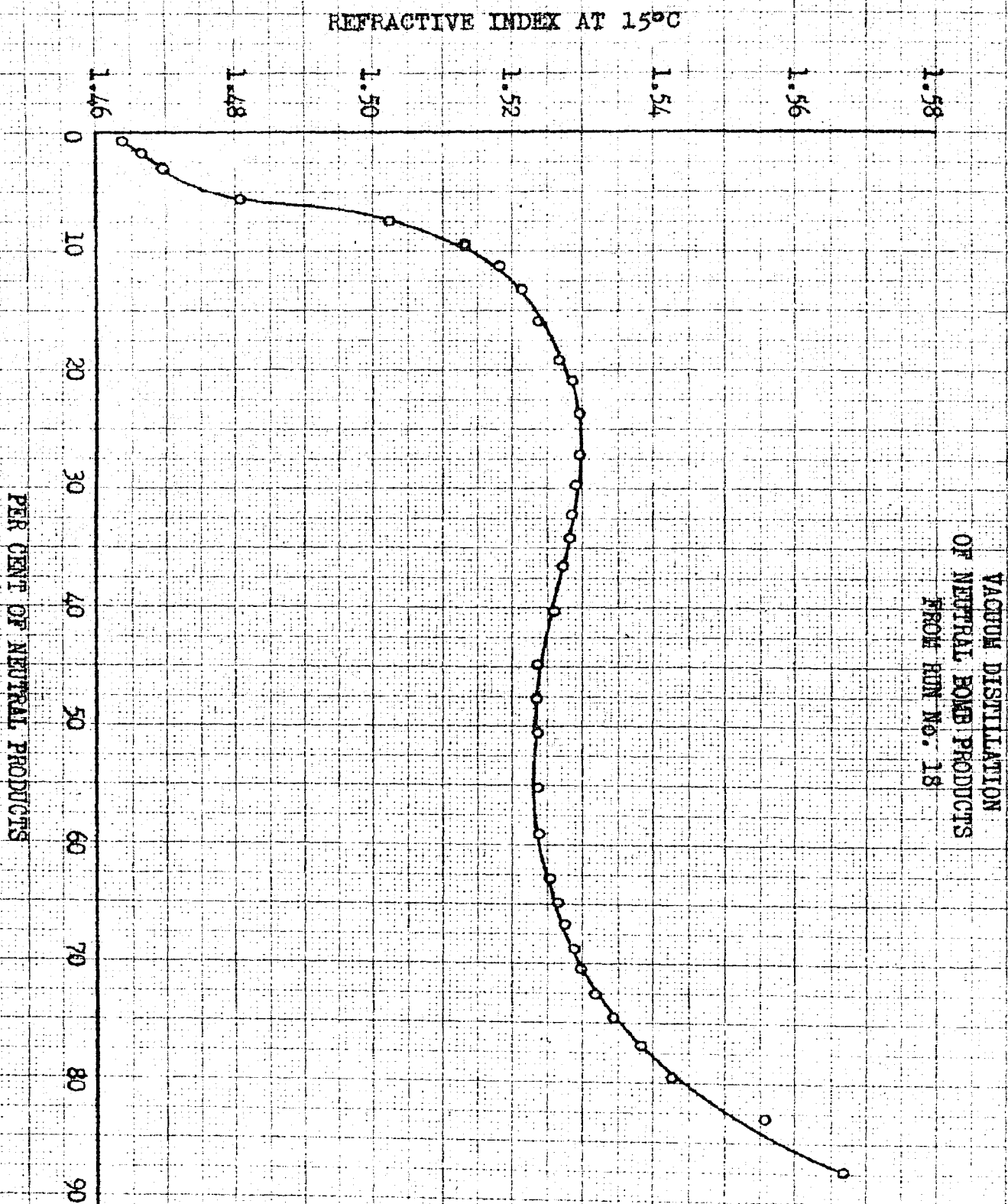


Fig. 19



VACUUM DISTILLATION
OF NEUTRAL BOMB PRODUCTS
FROM RUN No. 19



Fig. 21

Table V

Physical Constants of Purified Products
From Hydrogenating at 400°C
For different lengths of Time

Run Number	17	17	18	19
Product Isolated	1st	2nd	2nd	2nd
Density 20°/4°	0.942	0.938	0.943	0.942
R.I. 20°/D	1.5242	1.5194	1.5222	1.5238
Distillation range	122-8°C at 4 mm	127-30°C at 3 mm	127-31°C at 2 mm	146-55°C at 5 mm
% C	88.34 88.29	87.88 87.27	88.04 87.96	88.01 87.96
% H	11.43 11.42	12.03 12.07	11.77 11.72	11.78 11.81
Sp. Disp.	129.9	128.8	124.4	134.0

A redistillation of the first product isolated in run no. 17 resulted in three fractions of approximately 0.5 cc each. The densities and refractive indices of the fractions are listed below:

Fraction	Density 20°/ 4°	R.I. 20°/D
1	0.945	1.5250
2	0.943	1.5248
3	0.942	1.5243

From this data it appeared that there were possibly two isomers of the 12 methyldecahydroretene present, the one with the double bonds in conjugated positions the same as the one product identified under run no. 12 and the other with the double bonds in non-conjugated positions. If the ethylenic linkages were in conjugated positions and not connected to the isopropyl group the specific dispersion would be

137.4 but if they were non-conjugate the value would be 117.5. This is altogether possible since it has been previously determined that the one double bond in the original structure was saturated by treatment for 2 hours at 370°C and that dehydrogenation as well as alkyl decomposition occurred at 400°C. During the dehydrogenation it was quite possible that the hydrogen removal may result in the formation of either conjugate or non-conjugate double bonds. No attempt has been made to separate what was thought to be geometrical isomers of the other purified products.

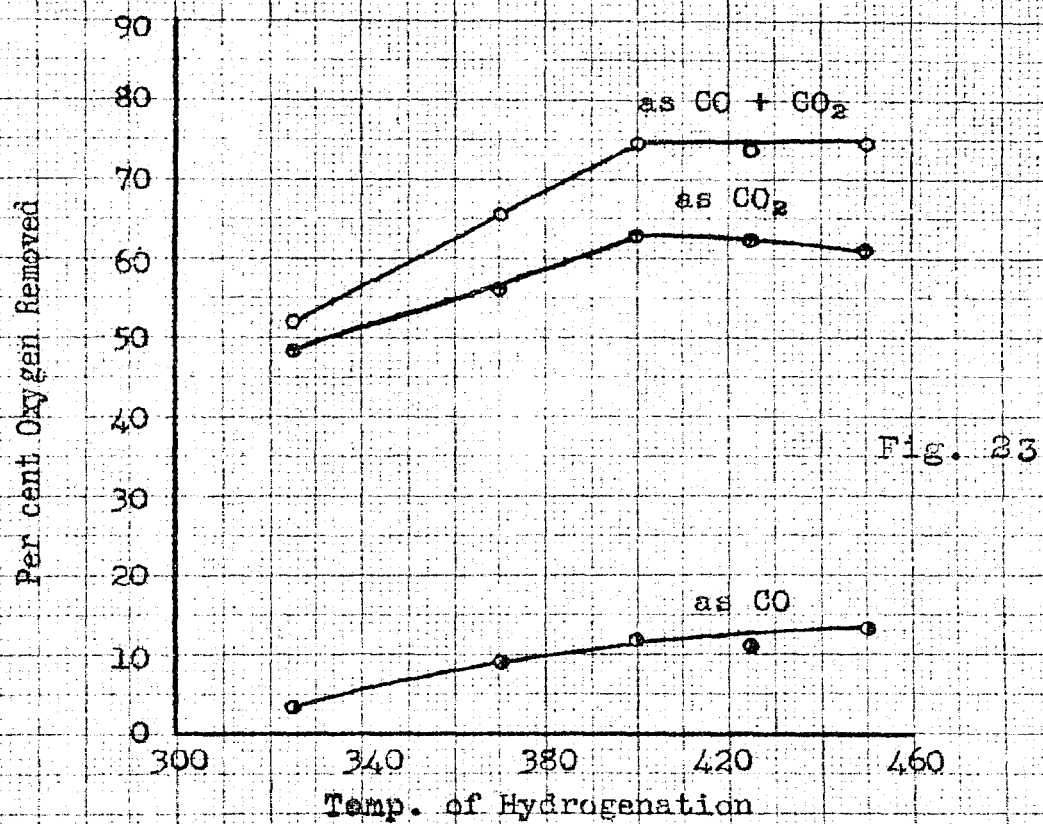
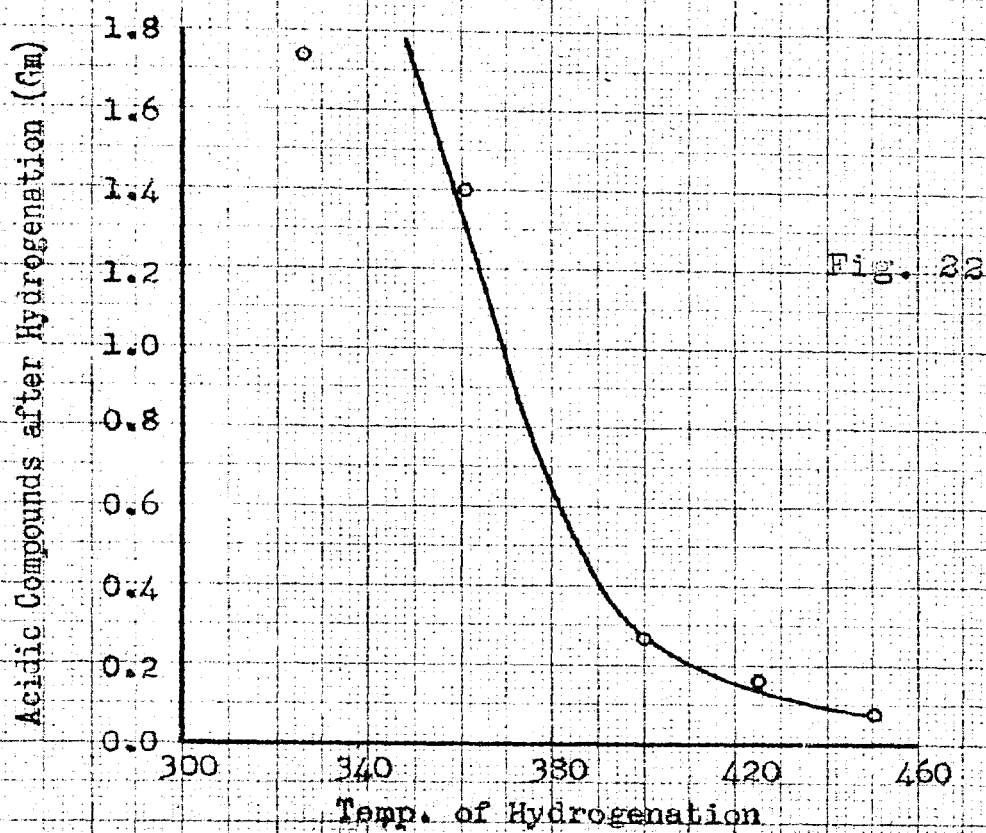
DISCUSSION OF THE RESULTS

The discussion of the results obtained by hydrogenating the abietic acid at different temperatures and for different lengths of time will be divided into four parts: (1) oxygen removal (2) alkyl decomposition (3) alicyclic decomposition and (4) hydrogen consumption. Under each part there will be included the results obtained by other workers in the field who have hydrogenated various compounds and the general application of all the results to coal hydrogenation.

OXYGEN REMOVAL

There are three types of oxygen containing compounds resulting from the hydrogenation experiments: (1) those which remain in the retort after the hydrogenation has been completed and the gaseous products removed, (2) water, which is removed with the gaseous products and then condensed in the traps, and (3) the gaseous compounds such as carbon monoxide and carbon dioxide.

By consulting figure 22 it is possible to obtain some idea concerning the amount of oxygen which remains in the retort. The curve shows the grams of acidic compounds as a function of the temperature of hydrogenation. It does not pass through the point obtained at 325°C because the curve is to represent the amount of oxygen and from this standpoint



the value given is misleading for two reasons. First of all, because it does not include the sodium salt which was found in the neutral products and which was due to the incomplete extraction of acidic compounds and second it does not include the iron abietate which was detected as an ether insoluble product. Although it is impossible to show exactly the number of grams of oxygen remaining in the retort due to the undetermined structure of a portion of the acids a fair estimate would be 10% of the weight of the acidic material since this is roughly the percent of oxygen in abietic acid and since the large majority of the acids is abietic.

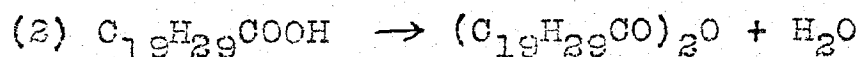
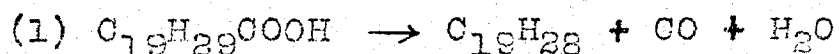
The amounts of acidic compounds which remain on hydrogenating the original acid at 400°C for one, two and three hours are 3.4 grams, 0.8 grams and 0.8 grams respectively. It may be noticed that the value of 0.8 grams is also the minimum value obtained at higher temperatures. Thus it may be concluded that there is apparently formed a relatively stable acid amounting to 0.8 grams. It may also be noticed that the grams of acids after 1 hour of hydrogenation are 3.4 grams as compared to 2.7 grams for 2 hours at the same temperature. This indicates that the destruction of the original acid occurs almost completely within the first hour.

Although it was impossible to determine quantitatively the amount of water formed during the reaction it is possible to obtain a rough approximation by measuring with

the aid of a graduated pipette the volume of water separated in trap No. 1. Based on this estimation the amounts of water formed during the reactions for 2 hours at different temperatures are as follows:

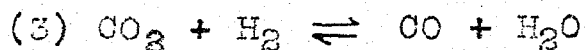
Temperature of Hydrogenation	Grams of H ₂ O formed
325°C	0.3
370°C	0.4
400°C	1.0
425°C	2.0
450°C	3.0

One possibility of water formation would be the reduction of the carboxyl group to form the aldehyde, the alcohol and eventually the hydrocarbon but there was no evidence whatsoever of any aldehydes or alcohols in the reaction products. LaLande (32) found the presence of water in the pyrolysis of the acid and explained it as a result of the following reactions:



Both of these reactions offer a possibility even though the presence of the anhydride was not established, for it may be possible that a small portion of the abietic acid identified in the retort products was formed from the anhydride during the extraction of the ether solution with the various aqueous solutions. However, it is believed that the large portion of abietic acid is present in the ether solution in the form of iron abietate.

The removal of oxygen from the abietic acid at different temperatures for 2 hours hydrogenation in the form of carbon dioxide and carbon monoxide is shown in table IV. This indicates that the percent of oxygen removed as $\text{CO}_2 + \text{CO}$ increases with temperature up to a value of about 75% at 400°C and then remains constant. However, the percent removed as CO_2 tends to decrease above 400°C with a corresponding increase in the percent removed as CO . This may best be shown by means of figure 23 on page 60. The reduction in the amount of CO_2 and the continual increase in the amount of CO tends to indicate that the reduction of CO_2 takes place according to the following reaction:



Eventhough the equilibrium constant for this reaction is quite low at the highest temperature of hydrogenation, the amounts of CO and H_2O would be appreciable due to the large amount of hydrogen. Such a reduction of carbon dioxide is suggested by Storch (50) to take place in the coal hydrogenation gases at high pressures.

The reduction of CO_2 is substantiated by the three one hour hydrogenations at 400°C . During the third hour of hydrogenation not even all of the CO_2 in the original hydrogen gas can be accounted for and yet there is formed an appreciable amount of CO . Thus it is concluded that the CO results from the reduction of the CO_2 in the original gas.

Table IV

Oxygen removal as Carbon Monoxide and Carbon Dioxide
Time of Hydrogenation - 2 hours

Run No.	Temp. of Hydrogenation	Grs. CO ₂ removed	Grs. O ₂ removed as CO ₂	% O ₂ removed as CO ₂	Grs. CO in gas	Grs. O ₂ removed as CO	% O ₂ removed as CO	Total Grs. O ₂ removed	% O ₂ removed
8	325	7.04	5.13	48.4	0.65	0.37	3.5	5.50	51.9
10	370	8.17	5.94	56.1	1.66	0.95	9.0	6.89	65.1
12	400	9.17	6.67	63.0	2.18	1.25	11.8	7.92	74.8
14	425	9.10	6.62	62.5	2.09	1.20	11.4	7.82	73.9
13	450	8.91	6.48	61.2	2.47	1.41	13.3	7.89	74.5

Table V

Oxygen removal as Carbon Monoxide and Carbon Dioxide
Temperature of Hydrogenation - 400°C

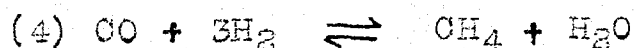
Run No.	Time of Hydrogenation	Grs. CO ₂ removed	Grs. O ₂ removed as CO ₂	% O ₂ removed as CO ₂	Grs. CO in gas	Grs. O ₂ removed as CO	% O ₂ removed as CO	Total Grs. O ₂ removed	% O ₂ removed
17	1 hour	8.90	6.47	61.1	2.22	1.27	12.0	7.74	73.1
18	2 hours	0.00	0.00	00.0	0.56	0.32	3.0	0.56	3.0
19	3 hours	0.00	0.00	00.0	0.19	0.11	1.0	0.19	1.0

With respect to the hydrogenations at 400°C for different lengths of time it may be seen from Table V that practically all of the oxygen is removed within the first hour. After that only a small percentage is removed in the form of carbon monoxide. This has been explained above.

From the theoretical yield of the reduction of CO₂ according to reaction (3) equal molar ratios of carbon monoxide and water should result. However, it may be noticed that at three higher temperatures there is a continual increase in the molar ratio of water to carbon monoxide:

Temperature of Hydrogenation	Molar Ratio H ₂ O to CO
400°C	0.72
435°C	1.48
450°C	1.90

This is explained due to the reduction of the carbon monoxide according to the equation 4.



Such a reaction is known to take place under these conditions and has been explained by the British Fuel Research Board.

Cawley (11) has studied the high pressure (100atmospheres) high temperature (450°C) hydrogenation of benzoic acid or ferrous benzoate and found that the acid was converted into 24% benzene and 41% toluene with a small amount (3%) of a higher boiling oil. At lower temperatures he found that dibenzyl (13-17%) was formed. He also found that the effect of catalysts for oxygen removal is small in comparison

to other oxygen containing structures such as phenols. In general he concludes that the carboxylic acids are less stable without a catalyst than the phenols. The present work agrees with his conclusions concerning the instability of the carboxyl group but the method by which it is destroyed appears to be quite different. In Cawley's work the presence of toluene indicates a reduction of the carboxyl group forming the aldehyde, alcohol and finally the hydrocarbon. However, it is believed that in the present work this type of reduction does not occur due to the presence of the stable methyl group attached to the same carbon as the carboxyl. This would thus tend to weaken the carbon to carbon linkage between the ring carbon and the carboxyl carbon and result in the splitting off of carbon dioxide.

Cawley (10) also hydrogenated phenol and cresols at 450°C and pressures of 100 atmospheres and found that they are fairly stable and only decomposed to the extent of about 6-8% after 2 hours. However in the presence of certain molybdenum catalysts they are almost completely deoxygenated. At higher temperatures (500°C) without a catalyst the OH group appears to be even more stable than the methyl and the tendency is for demethylation. The dihydric phenols are much less stable being decomposed into carbon, pitch and water.

Hall (24) hydrogenated α and β naphthols without a catalyst at 400°C and found that the α compound was deoxygenated

to the extent of 64% while the β was only 24% deoxygenated. At higher temperatures (450° and 500°C) both compounds were deoxygenated to the extent of about 70%.

Another type of oxygen containing compound to be hydrogenated is diphenylene oxide reported by the British Fuel Research Board (8). It has been found to be relatively stable under the hydrogenation-cracking conditions. At 450°C without a catalyst there was no conversion but with certain catalysts as high as 85% was converted into the following reaction products: benzene, cyclohexane and phenyl cyclohexane and at higher temperatures diphenyl.

In the 1938 report of the British Fuel Research Board (9) the results are presented for the hydrogenation-cracking of such oxygen containing compounds as o-phenylphenol and O,O'-diphenol. The first compound was completely deoxygenated at 300-340°C after prolonged treatment in the presence of a catalyst and it is suggested that the reaction probably proceeds similarly to that of phenol - partly by direct deoxygenation to diphenyl and partly by indirect formation of phenyl cyclohexane from phenyl cyclohexanol. The reaction products of the O,O' dihydroxydiphenyl are 6 to 17% diphenylene oxide and 3 to 8% o-phenylphenol after which decomposition occurs as discussed above for these compounds.

With respect to the removal of oxygen from coal by hydrogenation Bakes (2), Boomer (5), Graham (23) and Horton

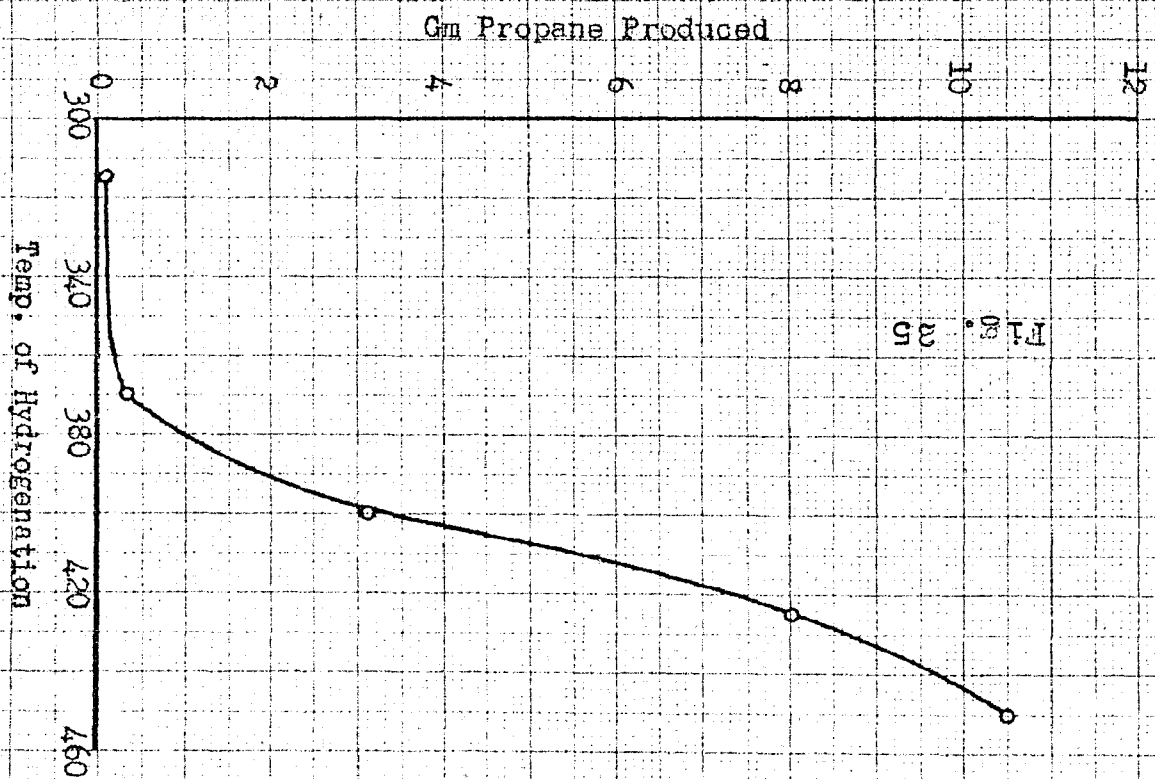
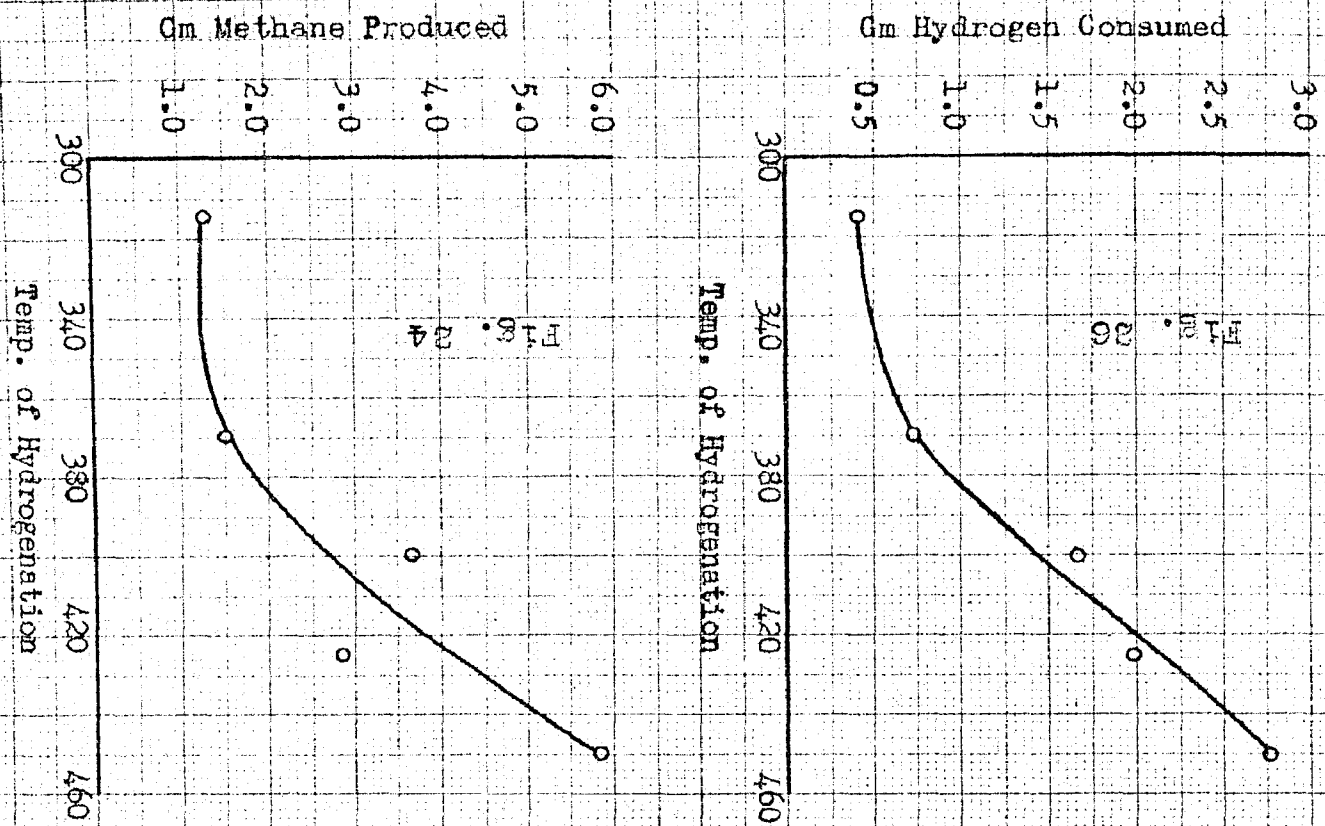
(27) were all able to show that much of the oxygen present in the coal is removed rapidly and in the early stages of hydrogenation and that the remaining oxygen is removed in a slow but rather constant rate. Later, Boomer (6) suggested a theory that coals contain at least two types of oxygen: oxygen as carboxyl which is removed rapidly and oxygen as hydroxyl which is more resistant. He explains that reduction of the carboxyl group to the aldehyde and the decomposition of the aldehyde is responsible for the formation of carbon monoxide. Fisher (20) supports the theory of two different types of oxygen but does not mention the types. He shows that 60% of the oxygen is eliminated much more rapidly than the remaining 40% and states that with a Pittsburgh coal most of the oxygen removed in the early stages appeared in the products as water. Storch (51) studied the oxygen removal in the anthraxylon fractions of various coals and found that the oxygen removed as CO_2 and water in the early stages increases with decreasing rank but that the removal of the remaining oxygen is about the same regardless of the rank. An extended study by Storch (49) revealed that the low rank coals, high in oxygen, lose much of it in the form of CO_2 instead of water.

On the basis of the present work it appears that the oxygen in coal which is rapidly removed by hydrogenation may be present in the carboxyl form and that any remaining oxygen is not likely to be present in this form.

ALKYL DECOMPOSITION

By the destructive hydrogenation of abietic acid it is possible to study the severence of two different alkyl groups from the parent phenanthrene structure. Both the removal of the two methyl groups located in different positions and the isopropyl group should offer some information regarding the removal of the same groups from coal if they are present.

In table II has been presented the results of the gaseous products formed during the reactions for two hours at different temperatures. By plotting the grams of methane obtained as a function of the temperature of hydrogenation (figure 24) it may be noticed that the amount increases slightly up to a temperature of approximately 380°C and then starts to increase rather sharply with temperature, indicating that the formation of methane is a function of temperature. By hydrogenating the acid at 400°C for one, two and three hours, 3 grams of methane are produced during the first hour, 1 gram during the second and 1 gram during the third. This indicates that the methane formation is dependent upon the time as well as the temperature of hydrogenation. For further evidence concerning the methane formation it may be recalled that in the identification of the predominating liquid products remaining after hydrogenation both methyl groups remained on the structure up to and including



the run at 400°C and that above this temperature the methyl group in the 13 position was severed from the phenanthrene structure. The removal of the methyl group in this position is in line with the dehydrogenation of the acid to form retene. However, even at 450°C this group is not entirely removed because if such were the case 5.3 grams of methane would result from this demethylation alone whereas altogether only 5.7 grams are obtained and some of this results from the reduction of carbon monoxide discussed under oxygen removal and the cracking of propane to be discussed later.

Figure 25 shows the result of propane formation as a function of temperature of hydrogenation. From 100 grams of abietic acid there are possible 14.6 grams of propane by complete removal of the isopropyl group and this value is approached rather rapidly above approximately 380°C . In fact above 400°C no products were identified which contained this group. By hydrogenating the acid at 400°C for one, two and three hours the amounts of propane obtained were 0.98 grams, 0.53 grams and 0.37 grams respectively as compared to a value of 3.12 grams for 2 hours of continuous hydrogenation. In other words more propane was obtained in two hours of continuous operation than in three hours of intermittent operation with fresh hydrogen being added at end of each hour. This would indicate that the removal of the isopropyl group is a function of the hydrogen concentration or partial pres-

sure of hydrogen or may be a function of the total pressure alone. However, under the conditions of the experiments the change in total pressure would be comparatively small to the change in partial pressure of hydrogen and thus it is believed that the stability of the isopropyl group is due to high partial pressure of hydrogen rather than the total pressure of the various gases.

The results of the Podbielniak distillation of the trapped gases from hydrogenating the acid at 400°C for 2 hours indicated the presence of ethane whereas the distillation of the gases obtained even after the third one hour period did not. This indicated that aside from the increased production of propane during the second hour of continuous operation the propane was cracked to form ethane and methane. This reaction is undoubtedly true for the higher temperatures of hydrogenation and thus indicates that the actual amount of depropylation is greater than shown in figure 25. So that it is quite possible that at 450°C practically all of the isopropyl group has been removed from the parent structure.

It is theoretically possible that all of the ethane produced from the various reactions results from the cracking of the propane. However this is not likely for some of it probably results from alicyclic decomposition to be discussed later.

The presence of iso- and normal butane in the gases indicate that cracking of the lower hydrocarbon gases to form olefins and the polymerization of the olefins probably takes place to form the C_4 compounds. However, the presence of any such olefins has not been detected in the gaseous products.

Another explanation of the n-butane would be a cracking of a saturated ring structure, such as ring number I with the result of an alkyl naphthlene. The alkyl group depending on its position of rupture could be either a pentyl or isopentyl group attached to the C_{11} or C_{12} position. This alkyl group could then be severed with the formation of n-butane and a methyl group attached to the naphthalene. This explanation, however does not account for the isobutane.

The British Fuel Research Board (54) has carried out the destructive hydrogenation of such compounds as α ,

β methyl and 2:6 dimethyl naphthalenes and found that the methyl groups are stable up to rather high temperatures. For example at 450°C the compounds are only demethylated to the extent of about 3% but at 500°C almost complete demethylation takes place. The 2:6 dimethyl compound is demethylated in stages yielding methyl naphthalene as an intermediate product.

At the present time there is no literature available concerning the higher hydrocarbon gases which are obtained as a result of coal hydrogenation because all the data presented in the technical literature are in terms of Orsat

analyses and thus the saturated hydrocarbons are reported as methane and ethane. The ethane values are probably in error because such gases undoubtedly contain higher hydrocarbons which may have resulted from alkyl groups originally present, from cracking and from polymerization of the low hydrocarbons or from a cracking of the alicyclic ring structures.

As a result of the present work it may be concluded that the removal of the alkyl groups attached to the parent structure depends upon the location of the group as well as the temperature, time and hydrogen pressure of the reactions. The methyl group is removed as methane and the isopropyl group is removed as propane. No evidence is available that indicates the isopropyl group is cracked before it is removed from the ring structure. It appears that the removal of the two groups studied does not start to any appreciable extent until a temperature of about 330°C has been reached. Below that temperature it may be noticed that the 13-methyl group appears to be removed faster than the isopropyl. This is undoubtedly due to the location of the group, so that no direct rule can be set up to claim that the removal of the alkyl groups is dependent upon the size of the group unless the comparison is made with both groups in the same position. Above 380°C it is obvious that the larger group (isopropyl) is removed more completely and more rapidly than the smaller (13-methyl). From the work no evidence has been found to indicate that the

1 methyl group has been removed to any appreciable extent which agrees with the experimental data of the British Fuel Research Board regarding the stability of an α or β methyl group.

ALICYCLIC DECOMPOSITION

At 370°C there is evidence of saturation of one of the two double bonds present in the original structure but at higher temperatures dehydrogenation takes place as indicated by the presence of two and three double bonds in the liquid products identified. This is even the case after a one hour period at 400°C. Since this type of dehydrogenation occurs, there is less tendency for alicyclic decomposition. Thus, it is believed that if a hydrogenation catalyst were present to prevent dehydrogenation more complete data on this type of reaction would be available.

However, an estimate concerning the extent of this type of decomposition may be obtained from the amount of products in the Podbielniak residue, in traps no. 1 and 2 (minus water) and in the low boiling products from the vacuum distillations. The low boiling material from the distillations represent the intermediate products while the low boiling material in the Podbielniak residue and condensable gases represent the final products of the decomposition.

The various amounts of the intermediate products have been estimated in terms of total products from the dis-

tillation curves to be about 3% at a hydrogenation temperature of 370°C, 17% at 400°C, 20% at 425°C and 25% at 450°C. Although none of these intermediate products has been definitely determined it may be stated that the refractive indices and boiling points show them to be related to the alkyl hydrogenaphthalenes. This would indicate a splitting of one of the three rings forming a naphthalene ring structure with an alkyl side chain. It is believed, based on the rules of cracking, that the saturated ring or ring no. 1 would be the one to be split.

The final products of alicyclic decomposition did not amount to more than approximately 10% of the total products even at the highest temperature of hydrogenation (450°C). However, the amounts of several of these products was such that it was possible to determine their chemical structures. They were found to be single ring structures consisting of 5 and 6 carbon atoms. Since there was no 5 membered ring to start with, these results indicate that isomerization must have taken place. Such an isomerization is described by independent workers (1) (9) who hydrogenated benzene under similar conditions and identified methylcyclopentane in the products. The presence of ethyl and methyl cyclohexane were also found in the products. The presence of the ethyl compound agrees with the theory of the British Fuel Research Board (7) concerning the alicyclic decomposition of naphthalene. The

theory states that one ring in the original naphthalene becomes saturated with hydrogen and then splits to form a n-butyl benzene which in turn cracks to form ethane and ethyl benzene. The ethyl benzene is then saturated to form ethyl cyclohexane. If this type of reaction occurs in the present work, and it is quite probable that it does, it would offer another source of ethane aside from the cracking of propane. The presence of the cyclohexene in these final products indicates that dehydrogenation occurs on the smaller compounds as well as the 3 ring structures.

Eventhough the present work has given little data concerning the actual mechanism of alicyclic decomposition of the phenanthrene structure due to the lack of data concerning the 2 ring structures, it may be of some value in explaining the nature of the oils resulting from coal hydrogenation. Biggs (3) (4) has shown that the oils resulting from the hydrogenation of Pittsburgh Coal are chiefly polycyclic hydroaromatic hydrocarbons and LeClaire (33) has found the same results with other coals. LeClaire's data indicates that the distillation fractions of such oils have refractive indices ranging from 1.4823 to 1.5710, densities ranging from 0.888 to 1.038 and specific dispersions ranging from 97.9 to 174.4. These values are within the range found in the present work which tends to indicate that the hydrogenation oils are possibly of a two or three ring structure.

HYDROGEN CONSUMPTION

Figure 26 on page 70 shows the grams of hydrogen consumed as a function of the hydrogenation temperature. From the curve it may be seen that as the temperature increases the hydrogen consumption increases slightly up to about 380°C and that above this temperature the consumption increases rather rapidly.

In all, there are three factors which effect the hydrogen consumption. These are: (1) absorption of hydrogen due to the double bonds, (2) consumption of hydrogen due to the alkyl and alicyclic decomposition, and (3) consumption of hydrogen due to the reduction of the oxides of carbon. The rather slow and continual increase in hydrogen consumption during the low temperatures is due principally to the saturation of hydrogen by the double bond. This is evident by the identification of a large amount of the dodecahydrophenanthrene derivative formed at 370°C. Above 380°C the relatively high hydrogen consumption is due to decomposition. This is deduced by the rapid increase in the formation of methane and propane and also in the amount of lower boiling material from the vacuum distillations. At the higher temperatures the increased consumption is due also to the reduction of CO and CO₂ as previously discussed.

Storch (49) (51) has studied the kinetics of hydrogen consumption on various samples of coal at 400°C in the absence of a catalyst and found that they all consumed hy-

drogen at approximately equal rates regardless of rank. The coals had oxygen contents ranging from 2.5 to 49.0% but this had practically no effect. The relation of the amount consumed to time was nearly linear for a period of twelve hours. This was not in agreement with the results in the present work obtained during the one, two and three hour period at 400°C. These results showed that only 0.48 grams of hydrogen were consumed during the first hour and practically no more was consumed after that. The comparison of this to the value at 400°C for two hours (1.67 grams consumed) verifies the fact that the hydrogen consumption is due in the case of abietic acid to the alkyl decomposition which takes place and suggests that in Storch's experiments the consumption is due principally to the saturation of the aromatic coal structure followed by alicyclic decomposition.

CONCLUSIONS

The destructive hydrogenation of abietic acid has been conducted for 2 hours with initial hydrogen pressures of 1900 to 1975 pounds per square inch at temperatures ranging between 325°C and 450°C; and for one, two and three hours intermittently with the same pressures at 400°C. From the results several conclusions have been obtained which are summarized below.

First of all, at least a portion of the original acid attacks the iron in the thermocouple or in the wall of the retort with the formation of iron abietate.

The amount of unconverted carboxyl material is quite appreciable (approximately 50%) at 325°C but decreases rather rapidly with an increase in hydrogenation temperature. For example, at 400°C only 2.8% of the carboxyl containing material remains after hydrogenation. This material is determined in the form of acidic compounds, principally abietic acid, but is believed to be removed from the retort in the form of the iron salt and possibly a small portion as the anhydride.

The destruction of the carboxyl group to form the oxides of carbon and water may occur by various possible methods, but the results indicate that, for the most part, it occurs as a straight decarboxylation with the formation of carbon dioxide and the corresponding hydrocarbon. The pre-

sence of the carbon monoxide and water is explained by the reduction of the carbon dioxide and finally, at the higher temperatures, the carbon monoxide is reduced to form methane and more water. In the cases where the oxygen is practically all removed approximately 75% of it appears in the oxides of carbon and 25% appears in the water. This decarboxylation is found to occur almost completely within the first hour of hydrogenation.

The alkyl decomposition of the compound is dependent upon the location and size of the group, the time and temperature of the reaction, and the partial pressure of the hydrogen. Of the two methyl groups present in the compound it is found that the one in the no. 1 position is relatively stable even under the most severe conditions studied, whereas the one in the no. 12 position is less stable. This group is removed rather slowly even at the low temperatures of hydrogenation but its removal increases more rapidly above 380°C. However, even at 450°C not all of the group has been removed. The hydrogenations for different lengths of time at 400°C indicate that the removal of this no. 12 methyl group is a function of time as well as temperature of hydrogenation.

The removal of the isopropyl group does not appear to any appreciable extent up to about 380°C but above this temperature the depropylation increases rather rapidly with temperature. At 450°C practically all of the isopropyl group

is removed. The intermittent hydrogenations show that the depropylation is a function of the partial pressure of hydrogen as well as the fact that the propene formed by depropylation is cracked to form ethane and methane.

The alicyclic decomposition of the hydrophenanthrene structure does not occur to any appreciable extent up to a hydrogenation temperature of 425°C but above this temperature the amount of decomposition increases rapidly. For example at 450°C approximately 75% of the three ring structure is destroyed. The first step in the alicyclic decomposition is the formation of alkyl hydronaphthalenes and the final step is the formation of one ring structures containing 5 and 6 carbon atoms. The 5 carbon ring indicates isomerization and presence of a cyclohexene indicates a dehydrogenation of the lower molecular weight compounds.

Finally, the slow but continual increase in hydrogen consumption with temperature up to about 380°C is due principally to the saturation of the double bonds, but, above this temperature the rapid increase in hydrogen consumption is due principally to the alkyl and alicyclic decomposition.

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Appendix I

Summary of Results
Time of Hydrogenation - 2 hours

	Grams		
Run No.	8	10	12
Temperature	325°C	370°C	400°C
Abietic Acid	100.00	100.00	100.00
Hydrogen Gas			
CO ₂	0.44	0.46	0.45
O ₂	0.73	0.77	0.76
CO	0.00	0.00	0.00
H ₂	12.94	13.51	13.41
CH ₄	0.31	0.33	0.33
N ₂	1.46	1.53	1.52
	15.88	16.60	16.47
Total Reactants	115.88	116.60	116.47
Retort Products			
Ether Insoluble	5.1	none	none
Acid Extracted	3.2	1.1	0.1
Alkaline Extracted	17.5	14.1	2.7
Neutral	62.8	67.6	68.9
	88.6	82.8	71.7
Condensable Gases			
Trap #1	0.75	0.93	2.21
Trap #2	0.63	0.67	0.45
Trap #3	7.48	8.63	9.62
	8.86	10.23	12.28
Podbielniak Gases			
Methane	0.02	0.02	0.44
Ethane	0.00	0.17	0.47
Propane	0.02	0.30	3.12
Isobutane	0.00	0.00	1.69
Butane	0.00	0.00	0.73
Residue	0.00	0.00	1.90
	0.04	0.49	8.35
Non-Condensable Gases			
CO ₂	0.00	0.00	0.00
O ₂	1.05	1.50	0.30
CO	0.65	1.66	2.36
H ₂	12.54	12.78	11.70
CH ₄	1.56	1.81	4.20
N ₂	0.92	0.68	0.43
	16.72	18.43	18.99
Total Products	114.22	111.95	111.32
Weight Loss	1.66	4.65	5.15

Appendix I (cont'd)

Summary of Results
Time of Hydrogenation - 2 hours

	Grams	
Run No.	14	13
Temperature	425°C	450°C
Abietic Acid	100.00	100.00
Hydrogen Gas		
CO ₂	0.45	0.45
O ₂	0.75	0.76
CO	0.00	0.00
H ₂	13.24	13.41
CH ₄	0.32	0.33
N ₂	1.50	1.52
	16.25	16.47
Total Reactants	116.25	116.47
Retort Products		
Ether Insoluble	none	none
Acid Extracted	0.4	trace
Alkaline Extracted	1.6	0.8
Neutral	59.4	47.7
	61.4	48.5
Condensable Gases		
Trap #1	4.34	5.99
Trap #2	2.71	4.00
Trap #3	9.54	9.36
	16.59	19.35
Podbielniak Gases		
Methane	0.77	2.98
Ethane	2.24	2.17
Propane	8.02	10.50
Isobutane	2.55	6.82
Butane	0.61	1.09
Residue	3.60	3.90
	17.79	27.46
Non-Condensable Gases		
CO ₂	0.00	0.00
O ₂	1.05	0.45
CO	2.09	2.47
H ₂	11.25	10.65
CH ₄	2.37	3.18
N ₂	0.39	0.69
	17.15	17.44
Total Products	112.93	112.75
Weight Loss	3.32	3.72

Appendix II

Summary of Results at 400°C

Grams

Run No.	17	18	19
Time	1st hour	2nd hour	3rd hour
Abietic Acid	100.00	100.00	100.00
Hydrogen Gas			
CO ₂	0.44	0.44	0.43
O ₂	0.74	0.74	0.74
CO	0.00	0.00	0.00
H ₂	13.13	13.10	13.98
CH ₄	0.32	0.32	0.31
N ₂	1.49	1.49	1.46
	16.12	16.09	15.92
Total Reactants	116.12	116.09	115.92
Retort Products			
Ether Insoluble	none	none	none
Acid Extracted	0.3	trace	trace
Alkaline Extracted	3.4	0.8	0.8
Neutral	78.4	76.6(1ow)	90.3
	82.10	81.5	91.10
Condensable Gases			
Trap #1	1.63	1.26	0.29
Trap #2	0.56	0.75	0.18
Trap #3	9.34	.47	0.22
	11.53	2.48	0.69
Podbielniak Gases			
Methane	0.41	0.00	0.00
Ethane	0.00	0.00	0.00
Propane	0.98	0.53	0.37
Isobutane	0.00	0.00	0.00
Butane	trace	trace	0.00
Residue	1.0	0.2	0.6
	2.39	0.73	0.97
Non-Condensable Gases			
CO ₂	0.00	0.00	0.00
O ₂	0.84	0.64	0.64
CO	2.22	0.56	0.19
H ₂	12.65	13.10	13.00
CH ₄	1.91	1.35	1.34
N ₂	1.14	1.38	1.35
	18.76	17.03	16.52
Total Products	114.78	101.74	109.28
Weight Loss	1.34	14.35	6.64